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PTO/SB/05 (4/98)

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1c965 U.S. PTO

**UTILITY  
PATENT APPLICATION  
TRANSMITTAL**

(Only for new nonprovisional applications under 37 CFR 1.53(b))

Attorney Docket No.	7575R&
First Inventor or Application Identifier	Mark Robert Sivik et al.
Title	COMPOSITIONS AND METHODS FOR USE OF ZWITTERIONIC POLYMERIC SUDS ENHANCERS
Express Mail Label No.	TB752810652US

1c938 U.S. PTO

09/30/2004

10/30/00

**APPLICATION ELEMENTS**  
See MPEP Chapter 600 concerning utility patent application contents.**ADDRESS TO:** Assistant Commissioner for Patents  
Box Patent Application  
Washington, D.C. 20231

1. ☒ \* Fee Transmittal Form (e.g., PTO/SB/17)  
(Submit an original, and a duplicate for fee processing)
2. ☒ Specification Total Pages [103]  
(preferred arrangement set forth below)
  - Descriptive Title of the Invention
  - Cross References to Related Applications
  - Statement Regarding Fed sponsored R&D
  - Reference to Microfiche Appendix
  - Background of the Invention
  - Brief Summary of the Invention
  - Brief Description of the Drawings (if filed)
  - Detailed Description
  - Claim(s)
  - Abstract of the Disclosure
3. ☐ Drawing(s) (35 USC 113) Total Sheets ☐
4. Oath or Declaration Total pages [2]
  - a. ☒ Newly executed (original or copy)
  - b. ☐ Copy from a prior application (37 CFR 1.63(d))  
(for continuation/divisional with Box 16 completed)
  - i. ☐ **DELETION OF INVENTORS**  
Signed statement attached deleting inventor(s) named in the prior application, see 37 CFR §§1.63(d)(2) and 1.33(b).

5. ☐ Microfiche Computer Program (Appendix)
6. Nucleotide and/or Amino Acid Sequence Submission  
(if applicable, all necessary)
  - a. ☐ Computer Readable copy
  - b. ☐ Paper Copy (identical to computer copy)
  - c. ☐ Statement verifying identity of above copies

**ACCOMPANYING APPLICATION PARTS**

7. ☐ Assignment Papers (cover sheet & document(s))
8. ☐ 37 CFR 3.73(b) Statement ☐ Power of Attorney  
(when there is an assignee)
9. ☐ English Translation Document (if applicable)
10. ☐ Information Disclosure ☐ Copies of IDS  
Statement (IDS)/PTO-1449 Citations
11. ☐ Preliminary Amendment
12. ☒ Return Receipt Postcard (MPEP 503)  
(Should be specifically itemized)
13. ☐ \*Small Entity ☐ Statement filed in prior application  
Statement(s) Status still proper and desired
14. ☐ Certified Copy of Priority Document(s)  
(if foreign priority is claimed)
15. ☐ Other: .....

**\* NOTE FOR ITEMS 1 & 13: IN ORDER TO BE ENTITLED TO PAY SMALL ENTITY FEES, A SMALL ENTITY STATEMENT IS REQUIRED (37. C.F.R. §1.27), EXCEPT IF ONE FILED IN A PRIOR APPLICATION IS RELIED UPON (37 C.F.R. §1.28).****16. If a CONTINUING APPLICATION**, check appropriate box and supply the requisite information below and in the preliminary amendment:☐ Continuation ☐ Divisional ☒ Continuation-in-part (CIP) of prior application No. 09/320,834 filed 05/26/99

Prior application information: Examiner: \_\_\_\_\_ Group/Art Unit: \_\_\_\_\_

For CONTINUATION or DIVISIONAL only: The entire disclosure of the prior application, from which a copy of the oath or declaration is supplied under Box 4b, is considered a part of the disclosure of the accompanying continuation or divisional application and is hereby incorporated by reference. The incorporation can only be relied upon when a portion has been inadvertently omitted from the submitted application parts.

**17. CORRESPONDENCE ADDRESS**☐ Customer Number or Bar Code Label

(Insert Customer No. or Attach bar code label here)

or ☐ Correspondence address below

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Signature		Date	October 30, 2000

Burden Hour Statement: This form is estimated to take 0.2 hours to complete. Time will vary depending upon the needs of the individual case. Any comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, Patent and Trademark Office, Washington, D.C. 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Assistant Commissioner for Patents, Box Patent Application, Washington, D.C. 20231.

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**FEE TRANSMITTAL  
for FY 2000**

Patent fees are subject to annual revision.  
Small Entity payments must be supported by a small entity statement,  
otherwise large entity fees must be paid. See Forms PTO/SB/09-12  
See 37 C.F.R. §§1.27 and 1.28.

**Complete if Known**

Application Number	
Filing Date	May 26, 1999
First Named Inventor	Mark Robert Sivik et al.
Examiner Name	
Group/Art Unit	1714
Attorney Docket No.	7575R&

**TOTAL AMOUNT OF PAYMENT (\$1,210.00)****METHOD OF PAYMENT (check one)**

1. ☒ The Commissioner is hereby authorized to charge indicated fees and credit any over payments to:

Deposit Account Number **16-2480**Deposit Account Name **The Procter & Gamble Company**

☒ Charge Any Additional Fee ☐ Charge the Issue Fee Set in  
Required Under 37 C.F.R. §1.18 at the Mailing  
37 C.F.R. §§1.16 and 1.17 of the Notice of Allowance

2. ☐ Payment Enclosed:  
☐ Check ☐ Money Order ☐ Other

**FEE CALCULATION****1. BASIC FILING FEE**

Large Code	Entity Fee (\$)	Small Code	Entity Fee (\$)	Fee Description	Fee Paid
101	690	201	345	Utility filing fee	[\$710]
106	310	206	155	Design filing fee	
107	480	207	240	Plant filing fee	
108	690	208	345	Reissue filing fee	
114	150	214	75	Provisional filing fee	
<b>SUBTOTAL (1)</b>					<b>(\$)[710.00]</b>

**2. EXTRA CLAIM FEES**

Fee From  
Extra Claims Below Fee

Paid  
Total Claims [30] - 20\*\* = [10] x [18] = [180]  
Independent Claims [7] - 3\*\* = [4] x [80] = [320]  
Multiple Dependent ☐ = ☐  
\*\* or number previously paid, if greater, For Reissues, see below

Large Code	Entity Fee (\$)	Small Code	Entity Fee (\$)	Fee Description	Fee Paid
103	18	203	9	Claims in excess of 20	
102	78	202	39	Independent claims in excess of 3	
104	260	204	130	Multiple dependent claim, if not	
109	78	209	39	**Reissue independent claims over original patent	
110	18	210	9	**Reissue claims in excess of 20 and over original patent	

**SUBTOTAL (2) (\$)[500]****FEE CALCULATION (continued)****3. ADDITIONAL FEES**

Large Code	Entity Fee (\$)	Small Code	Entity Fee (\$)	Fee Description	Fee
105	130	205	65	Surcharge - late filing fee or oath	<input type="checkbox"/>
127	50	227	25	Surcharge - late provisional filing fee or cover sheet	<input type="checkbox"/>
139	130	139	130	Non-English specification	<input type="checkbox"/>
147	2,520	147	2,520	For filing a request for reexamination	<input type="checkbox"/>
112	920*	112	920*	Requesting publication of SIR prior to Examiner's action	<input type="checkbox"/>
113	1,840*	113	1,840*	Requesting publication of SIR after Examiner's action	<input type="checkbox"/>
115	110	215	55	Extension for reply within 1 <sup>st</sup> month	<input type="checkbox"/>
116	380	216	190	Extension for reply within 2 <sup>nd</sup> month	<input type="checkbox"/>
117	870	217	435	Extension for reply within 3 <sup>rd</sup> month	<input type="checkbox"/>
118	1,360	218	680	Extension for reply within 4 <sup>th</sup> month	<input type="checkbox"/>
128	1,850	228	925	Extension for reply within 5 <sup>th</sup> month	<input type="checkbox"/>
119	300	219	150	Notice of Appeal	<input type="checkbox"/>
120	300	220	150	Filing a brief in support of an appeal	<input type="checkbox"/>
121	260	221	130	Request for oral hearing	<input type="checkbox"/>
138	1,510	138	1,510	Petition to institute a public use proceeding	<input type="checkbox"/>
140	110	240	55	Petition to revive - unavoidable	<input type="checkbox"/>
141	1,210	241	605	Petition to revive - unintentional	<input type="checkbox"/>
142	1,210	242	605	Utility issue fee (or reissue)	<input type="checkbox"/>
143	430	243	215	Design issue fee	<input type="checkbox"/>
144	580	244	290	Plant issue fee	<input type="checkbox"/>
122	130	122	130	Petitions to the Commissioner	<input type="checkbox"/>
123	50	123	50	Petitions related to provisional applications	<input type="checkbox"/>
126	240	126	240	Submission of IDS	<input type="checkbox"/>
581	40	581	40	Recording each patent assignment per property (times number of properties)	<input type="checkbox"/>
146	690	246	345	Filing a submission after final rejection	<input type="checkbox"/>
149	690	249	345	For each additional invention to be examined (37 CFR 1.129(b))	<input type="checkbox"/>

Other fee (specify) \_\_\_\_\_ ☐

Other fee (specify) \_\_\_\_\_ ☐

**\* Reduced by Basic Filing Fee Paid SUBTOTAL(3) (\$) [0]****SUBMITTED BY**

Kevin L. Waugh

Registration  
No.  
(Attorney/Agent)

47,206

**Complete (if applicable)**

Telephone (513) 627-1644

Name (Print/Type)

Signature

Date 10/30/00

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**COMPOSITIONS AND METHODS FOR USING  
ZWITTERIONIC POLYMERIC SUDS ENHANCERS**

Mark Robert Sivik

Jean Francois Bodet

Bernard William Kluesener

William Michael Scheper

Dominic Wai-Kwing Yeung

Vance (nmn) Bergeron

**RELATED APPLICATIONS**

This application is a continuation-in-part application of U.S. Application Serial No. 09/320,834 filed May 26, 1999, which is incorporated herein by reference in its entirety.

**FIELD OF THE INVENTION**

The present invention relates to methods for using zwitterionic polymeric suds enhancers (stabilizers) to increase the suds and/or foam volume and suds and/or foam retention in suds-forming and/or foam-forming compositions comprising such zwitterionic polymeric suds stabilizers. Suitable suds-forming and/or foam-forming compositions comprise one or more zwitterionic polymeric suds stabilizers.

**BACKGROUND OF THE INVENTION**

Suds-forming and/or foam-forming compositions are well known. Such compositions require a suds-forming component and/or foam-forming component. Polymeric materials are one example of such suds-forming components and/or foam-forming components.

Formulators have been attempting unsuccessfully to develop better performing polymeric materials for use as suds-forming and/or foam-forming components.

Accordingly, there remains a need in the art for polymeric materials useful as suds-forming and/or foam-forming components suitable for suds-forming and/or foam-forming compositions which exhibit increased suds and/or foam volume and suds and/or foam retention. The need exists for a composition which can maintain a high level of suds and/or foam as long as the suds-forming and/or foam-forming composition is effective for its purpose.

**SUMMARY OF THE INVENTION**

The present invention meets the aforementioned needs in that it has been surprisingly discovered that certain zwitterionic polymeric materials serve as suds and/or foam extenders and suds and/or foam volume enhancers in suds-forming and/or foam-forming compositions.

5       The zwitterionic polymeric suds stabilizers of the present invention comprise monomeric units which have at least one moiety capable of sustaining a negative charge at a pH of from about 4 to about 12 and at least one moiety capable of sustaining a positive charge within the same pH range.

10       The present invention relates to a method for providing increased suds volume and increased suds retention in suds-forming and/or foam-forming compositions, other than liquid dishwashing compositions, such as personal care compositions (i.e., shampoos, hand washing compositions, body washing composition, hair removal compositions, etc.), laundry detergent compositions, especially laundry bars and/or high suds phosphate  
15       compositions, hard surface cleaning compositions, agrochemical foaming compositions, oil-field foaming compositions and/or fire-fighting foaming compositions.

20       In one aspect, a method for providing increased suds volume and increased suds retention while washing parts of a person's body, such as hair, hands, other parts of the body, in need of cleaning, comprising the step of contacting said parts with an aqueous solution of a personal care composition, said personal care composition comprising:

- a) an effective amount of a zwitterionic polymeric suds stabilizer as hereinafter defined;
- b) an effective amount of a deterative surfactant; and
- c) balance carriers and other adjunct ingredients;

25       provided that the pH of a 10% aqueous solution of said personal care composition is from about 4 to about 12, is provided.

30       In another aspect, a method for providing increased suds volume and increased suds retention while washing, preferably by hand, a fabric and/or garment in need of cleaning, comprising the step of contacting said fabric and/or garment with an aqueous solution of a laundry detergent composition, said laundry detergent composition comprising:

- a) an effective amount of a polymeric suds stabilizer as hereinafter defined;
- b) an effective amount of a deterative surfactant; and
- c) balance carriers and other adjunct ingredients;

35       provided that the pH of a 10% aqueous solution of said laundry detergent

composition is from about 4 to about 12, is provided.

In yet another aspect, a method for providing increased suds volume and increased suds retention while cleaning a hard surface, such as a countertop, tile floors, bathroom fixtures, bathtubs, showers, toilets, etc., in need of cleaning in need of cleaning,  
5 comprising the step of contacting said hard surface with an aqueous solution of a hard surface cleaning composition, said hard surface cleaning composition comprising:

- a) an effective amount of a polymeric suds stabilizer as hereinafter defined;
- b) an effective amount of a deterative surfactant; and
- 10 c) balance carriers and other adjunct ingredients;

provided that the pH of a 10% aqueous solution of said hard surface cleaning composition is from about 4 to about 12, is provided.

In still yet another aspect, a method for providing increased su45  
ds volume and increased suds retention while treating a plant and/or crop in need  
15 of treatment, comprising the step of contacting said plant and/or crop with an aqueous solution of a agrochemical foaming composition, said agrochemical foaming composition comprising:

- a) an effective amount of a polymeric suds stabilizer as hereinafter defined;
- 20 b) an effective amount of a deterative surfactant; and
- c) balance carriers and other adjunct ingredients;

provided that the pH of a 10% aqueous solution of said agrochemical foaming composition is from about 4 to about 12, is provided.

In still yet another aspect, a method for providing increased suds volume and  
25 increased suds retention while drilling for oil in oil-fields, comprising the step of contacting said drilling equipment and/or subterranean formations with an aqueous solution of a oil-field foaming composition, said oil-field foaming composition comprising:

- a) an effective amount of a polymeric suds stabilizer as hereinafter defined;
- 30 b) an effective amount of a clay; and
- c) balance carriers and other adjunct ingredients;

provided that the pH of a 10% aqueous solution of said oil-field foaming composition is from about 4 to about 12, is provided.

35 In still yet another aspect, a method for providing increased suds volume and increased suds retention while fighting a fire, comprising the step of contacting said fire

with an aqueous solution of a fire-fighting foaming composition, said fire-fighting foaming composition comprising:

- a) an effective amount of a polymeric suds stabilizer as hereinafter defined;
- b) an effective amount of a deterative surfactant; and
- c) balance carriers and other adjunct ingredients;

provided that the pH of a 10% aqueous solution of said fire-fighting foaming composition is from about 4 to about 12, is provided.

These and other objects, features and advantages will become apparent to those of ordinary skill in the art from a reading of the following detailed description and the appended claims.

All percentages, ratios and proportions herein are by weight, unless otherwise specified. All temperatures are in degrees Celsius (°C) unless otherwise specified. All documents cited are in relevant part, incorporated herein by reference.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to zwitterionic polymeric materials which provide enhanced suds and/or foam duration and enhanced suds and/or foam volume when formulated into suds-forming and/or foam-forming compositions. The zwitterionic polymers of the present invention may be homopolymers or copolymers, each of which may be suitably crosslinked. The zwitterionic polymers are comprised of moieties which when placed in an aqueous solution having a pH of from 4 to about 12, said moieties are capable of sustaining a positive or negative charge.

The suds-forming and/or foam-forming compositions of the present invention have a pH of from about 4 to about 12 when measured as a 10% aqueous solution. The polymeric suds enhancers of the present invention are zwitterionic polymers. For the purposes of the present invention the term "zwitterionic polymer" is defined as "a polymeric material comprised of one or more monomers wherein each monomer has one or more moieties capable of sustaining a positive or negative charge at a pH of from about 4 to about 12 such that the number of positively charged moieties is equal to the number of negatively charged moieties at the isoelectric point of said polymer."

The compositions according to the present invention also comprise an effective amount of one or more deterative surfactants described herein below as well as carriers and other adjunct ingredients.

The suds-forming and/or foam-forming compositions of the present invention comprise:

- a) an effective amount of a zwitterionic polymeric suds stabilizer; and
- b) optionally an effective amount of a deterative surfactant or clay; and
- c) the balance carriers and other adjunct ingredients;

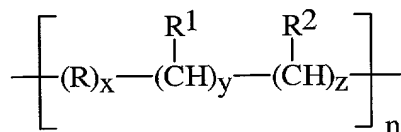
provided that a 10% aqueous solution of said composition has a pH of from about 4 to about 12.

The following describe non-limiting examples of polymeric material which may be suitable for use in the suds-forming and/or foam-forming compositions of the present invention.

#### Zwitterionic Polymers

The polymeric suds stabilizers of the present invention are homopolymers or copolymers wherein the monomers which comprise said homopolymers or copolymers contain a moiety capable of being protonated at a pH of from about 4 to about 12, or a moiety capable of being de-protonated at a pH of from about 4 to about 12, of a mixture of both types of moieties.

A preferred class of zwitterionic polymer suitable for use as a suds volume and suds duration enhancer has the formula:

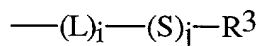


wherein R is C<sub>1</sub>-C<sub>12</sub> linear alkylene, C<sub>1</sub>-C<sub>12</sub> branched alkylene, and mixtures thereof; preferably C<sub>1</sub>-C<sub>4</sub> linear alkylene, C<sub>3</sub>-C<sub>4</sub> branched alkylene; more preferably methylene and 1,2-propylene. R<sup>1</sup> and R<sup>2</sup> are defined herein after. The index x is from 0 to 6; y is 0 or 1; z is 0 or 1.

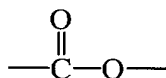
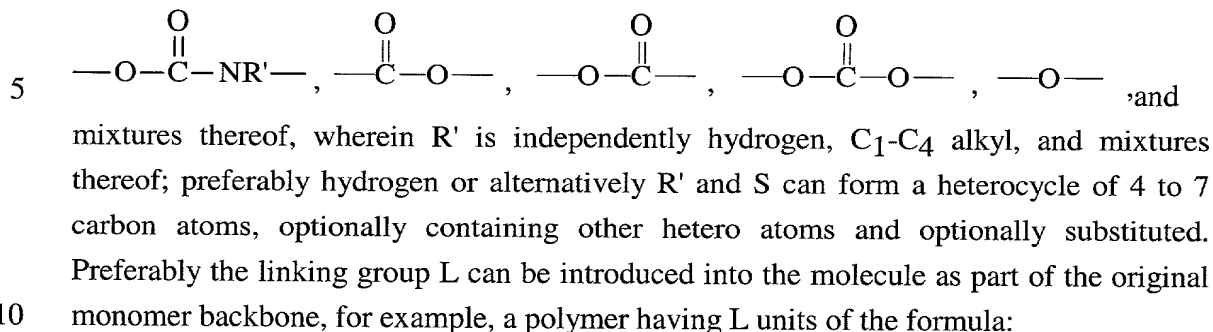
The index n has the value such that the zwitterionic polymers of the present invention have an average molecular weight of from about 1,000 to about 2,000,000 preferably from about 5,000 to about 1,000,000, more preferably from about 10,000 to about 750,000, more preferably from about 20,000 to about 500,000, even more preferably from about 35,000 to about 300,000 daltons. The molecular weight of the polymeric suds boosters, can be determined via conventional gel permeation chromatography.

#### Anionic Units

R<sup>1</sup> is a unit capable of having a negative charge at a pH of from about 4 to about 12. Preferred R<sup>1</sup> has the formula:

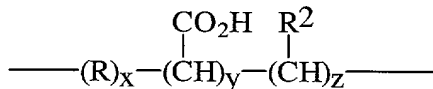


wherein L is a linking unit independently selected from the following:



can suitably have this moiety introduced into the polymer via a carboxylate containing monomer, for example, a monomer having the general formula:

15



When the index i is 0, L is absent.

For anionic units S is a "spacing unit" wherein each S unit is independently selected from C<sub>1</sub>-C<sub>12</sub> linear alkylene, C<sub>1</sub>-C<sub>12</sub> branched alkylene, C<sub>3</sub>-C<sub>12</sub> linear alkenylene, C<sub>3</sub>-C<sub>12</sub> branched alkenylene, C<sub>3</sub>-C<sub>12</sub> hydroxyalkylene, C<sub>4</sub>-C<sub>12</sub> dihydroxyalkylene, C<sub>6</sub>-C<sub>10</sub> arylene, C<sub>8</sub>-C<sub>12</sub> dialkylarylene,  $\text{---(R}^5\text{O)}_k\text{R}^5\text{---}$ ,  $\text{---(R}^5\text{O)}_k\text{R}^6\text{(OR}^5)_k\text{---}$ ,  $\text{---CH}_2\text{CH(OR}^7\text{)CH}_2\text{---}$ , and mixtures thereof; wherein R<sup>5</sup> is C<sub>2</sub>-C<sub>4</sub> linear alkylene, C<sub>3</sub>-C<sub>4</sub> branched alkylene, and mixtures thereof, preferably ethylene, 1,2-propylene, and mixtures thereof, more preferably ethylene; R<sup>6</sup> is C<sub>2</sub>-C<sub>12</sub> linear alkylene, and mixtures thereof, preferably ethylene; R<sup>7</sup> is hydrogen, C<sub>1</sub>-C<sub>4</sub> alkyl, and mixtures thereof, preferably hydrogen. The index k is from 1 to about 20.

25

Preferably S is C<sub>1</sub>-C<sub>12</sub> linear alkylene,  $\text{---(R}^5\text{O)}_k\text{R}^5\text{---}$ , and mixtures thereof. When S is a  $\text{---(R}^5\text{O)}_k\text{R}^5\text{---}$  unit, said units may be suitably formed by the addition an alkyleneoxy producing reactant (e.g. ethylene oxide, epichlorohydrin) or by addition of a suitable polyethyleneglycol. More preferably S is C<sub>2</sub>-C<sub>4</sub> linear alkylene. When the index j is 0 the S unit is absent.

30



R<sup>3</sup> is independently selected from hydrogen, -CO<sub>2</sub>M, -SO<sub>3</sub>M, -OSO<sub>3</sub>M, -CH<sub>2</sub>P(O)(OM)<sub>2</sub>, -OP(O)(OM)<sub>2</sub>, units having the formula:

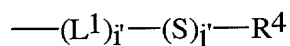


- 5 wherein each R<sup>8</sup>, R<sup>9</sup>, and R<sup>10</sup> is independently selected from the group consisting of hydrogen, -(CH<sub>2</sub>)<sub>m</sub>R<sup>11</sup>, and mixtures thereof, wherein R<sup>11</sup> is -CO<sub>2</sub>H, -SO<sub>3</sub>M, -OSO<sub>3</sub>M, -CH(CO<sub>2</sub>H)CH<sub>2</sub>CO<sub>2</sub>H, -CH<sub>2</sub>P(O)(OH)<sub>2</sub>, -OP(O)(OH)<sub>2</sub>, and mixtures thereof, preferably -CO<sub>2</sub>H, -CH(CO<sub>2</sub>H)CH<sub>2</sub>CO<sub>2</sub>H, and mixtures thereof, more preferably -CO<sub>2</sub>H; provided that one R<sup>8</sup>, R<sup>9</sup>, or R<sup>10</sup> is not a hydrogen atom, preferably two R<sup>8</sup>, R<sup>9</sup>, or R<sup>10</sup> units are hydrogen. M is hydrogen or a salt forming cation, preferably hydrogen.
- 10 The index m has the value from 0 to 10.

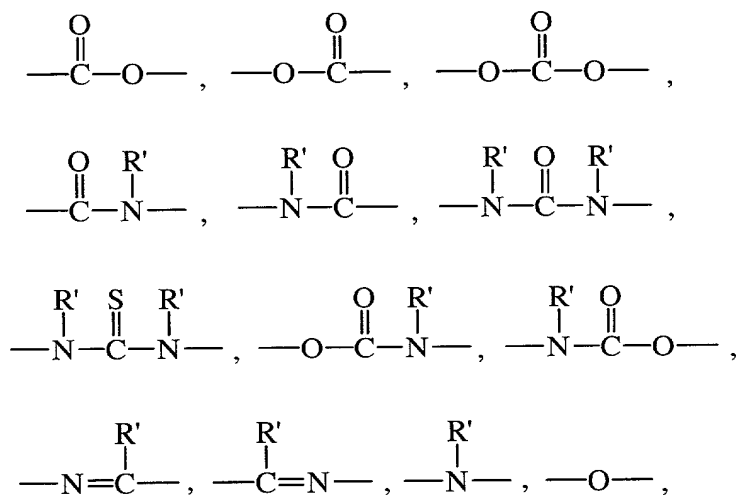
Cationic Units

R<sup>2</sup> is a unit capable of having a positive charge at a pH of from about 4 to about 12. Preferred R<sup>2</sup> has the formula:

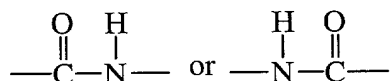
15



wherein L<sup>1</sup> is a linking unit independently selected from the following:



- 20 and mixtures thereof; wherein R' is independently hydrogen, C<sub>1</sub>-C<sub>4</sub> alkyl, and mixtures thereof; preferably hydrogen or alternatively R' and S can form a heterocycle of 4 to 7 carbon atoms, optionally containing other hetero atoms and optionally substituted. Preferably L<sup>1</sup> has the formula:



When the index i' is equal to 0, L<sup>1</sup> is absent.

For cationic units S is a "spacing unit" wherein each S unit is independently selected from C<sub>1</sub>-C<sub>12</sub> linear alkylene, C<sub>1</sub>-C<sub>12</sub> branched alkylene, C<sub>3</sub>-C<sub>12</sub> linear alkenylene, C<sub>3</sub>-C<sub>12</sub> branched alkenylene, C<sub>3</sub>-C<sub>12</sub> hydroxyalkylene, C<sub>4</sub>-C<sub>12</sub> dihydroxyalkylene, C<sub>6</sub>-C<sub>10</sub> arylene, C<sub>8</sub>-C<sub>12</sub> dialkylarylene, -(R<sup>5</sup>O)<sub>k</sub>R<sup>5</sup>-, -(R<sup>5</sup>O)<sub>k</sub>R<sup>6</sup>(OR<sup>5</sup>)<sub>k</sub>-, -CH<sub>2</sub>CH(OR<sup>7</sup>)CH<sub>2</sub>-, and mixtures thereof; wherein R<sup>5</sup> is C<sub>2</sub>-C<sub>4</sub> linear alkylene, C<sub>3</sub>-C<sub>4</sub> branched alkylene, and mixtures thereof, preferably ethylene, 1,2-propylene, and mixtures thereof, more preferably ethylene; R<sup>6</sup> is C<sub>2</sub>-C<sub>12</sub> linear alkylene, and mixtures thereof, preferably ethylene; R<sup>7</sup> is hydrogen, C<sub>1</sub>-C<sub>4</sub> alkyl, and mixtures thereof, preferably hydrogen. The index k is from 1 to about 20.

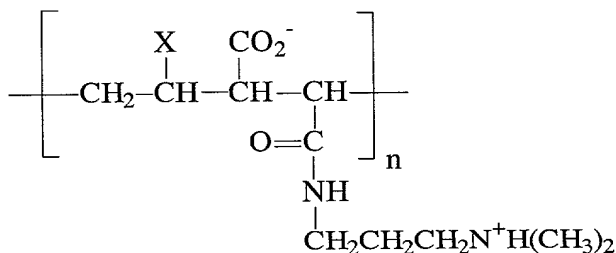
Preferably S is C<sub>1</sub>-C<sub>12</sub> linear alkylene, and mixtures thereof. Preferably S is C<sub>2</sub>-C<sub>4</sub> linear alkylene. When the index j' is 0 the S unit is absent.

R<sup>4</sup> is independently selected from amino, alkylamino carboxamide, 3-imidazolyl, 4-imidazolyl, 2-imidazolyl, 4-imidazolyl, 2-piperidinyl, 3-piperidinyl, 4-piperidinyl, 1-pyrazolyl, 3-pyrazolyl, 4-pyrazolyl, 5-pyrazolyl, 1-pyrazolyl, 3-pyrazolyl, 4-pyrazolyl, 5-pyrazolyl, 2-pyridinyl, 3-pyridinyl, 4-pyridinyl, piperazinyl, 2-pyrrolidinyl, 3-pyrrolidinyl, guanidino, amidino, and mixtures thereof, preferably dialkylamino having the formula:



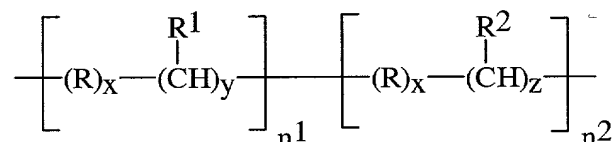
wherein each R<sup>11</sup> is independently hydrogen, C<sub>1</sub>-C<sub>4</sub> alkyl, and mixtures thereof, preferably hydrogen or methyl or alternatively the two R<sup>11</sup> can form a heterocycle of 4 to 8 carbon atoms, optionally containing other hetero atoms and optionally substituted.

An example of a preferred zwitterionic polymer according to the present invention has the formula:



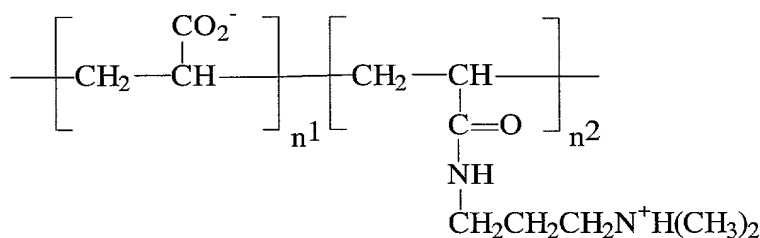
wherein X is C<sub>6</sub>, n has a value such that the average molecular weight is from about 5,000 to about 1,000,000 daltons.

Further preferred zwitterionic polymers according to the present invention are polymers comprising monomers wherein each monomer has only cationic units or anionic units, said polymers have the formula:



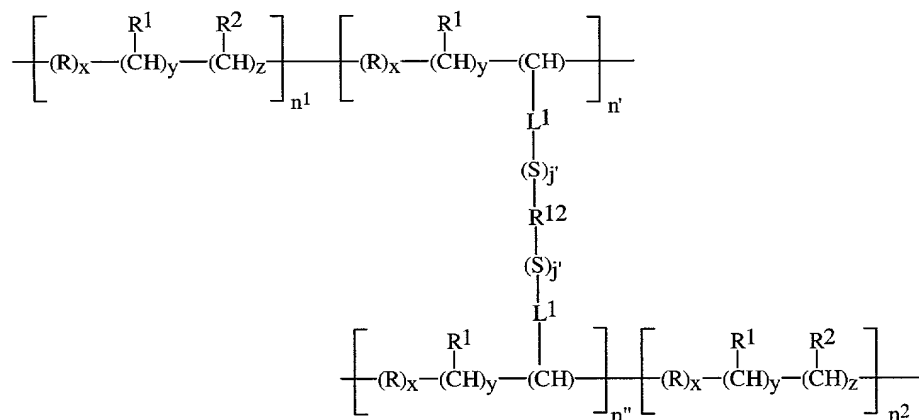
wherein R, R<sup>1</sup>, x, y, and z are the same as defined herein above; n<sup>1</sup> + n<sup>2</sup> = n such that n has a value wherein the resulting zwitterionic polymer has a molecular weight of form about 5,000 to about 1,000,000 daltons.

An example of a polymer having monomers with only an anionic unit or a cationic unit has the formula:



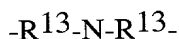
wherein the sum of n<sup>1</sup> and n<sup>2</sup> provide a polymer with an average molecular weight of from about 5,000 to about 750,000 daltons.

Another preferred zwitterionic polymer according to the present invention are polymers which have limited crosslinking, said polymers having the formula:



wherein R, R<sup>1</sup>, L<sup>1</sup>, S, j', x, y, and z are the same as defined herein above; n' is equal to n", and the value n' + n" is less than or equal to 5% of the value of n<sup>1</sup> + n<sup>2</sup> = n; n provides a polymer with an average molecular weight of from about 1,000 to about 2,000,000 daltons. R<sup>12</sup> is nitrogen, C<sub>1</sub>-C<sub>12</sub> linear alkylene amino alkylene having the formula:

5



L<sup>1</sup>, and mixtures thereof, wherein each R<sup>13</sup> is independently L<sup>1</sup> or ethylene.

The zwitterionic polymers of the present invention may comprise any combination of monomer units, for example, several different monomers having various R<sup>1</sup> and R<sup>2</sup> groups can be combined to form a suitable suds stabilizer. Alternatively the same R<sup>1</sup> unit may be used with a selection of different R<sup>2</sup> units and vice versa.

A particular process may be advantageous to make copolymers from at least one tertiary amino-containing monomer, e.g., dimethylaminoethyl(meth)acrylate, and at least one vinyl-containing monomer, when the at least one vinyl-functional monomer is not substituted by an alkyl group on the 2-position of the vinyl moiety (for example, not methacrylic acid, hydroxyethylmethacrylate or hydroxypropylmethacrylate). This is advantageous to make such copolymers free of or having minimal Michael addition adducts of the ingredients. Also, Michael addition adducts form but revert back to monomers if the hydrogen atom is substituted by an alkyl group on the 2-position of the vinyl moiety.

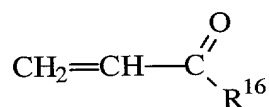
In the process, at least one tertiary amino-containing monomer, at least one vinyl-containing monomer not substituted by an alkyl group on the 2-position of the vinyl moiety, an acid, and a polymerization initiator are mixed in a polymerization reactor to form a polymerization mixture in the reactor. The at least one tertiary amino-containing monomer and the at least one vinyl-containing monomer are copolymerized in the polymerization mixture, to form a copolymer, and optionally a Michael addition adduct of the at least one tertiary amino-containing monomer and the at least one vinyl-containing monomer. However, Michael adduct formation is prevented/minimized by performing at least one of the following steps in a process for making copolymers from tertiary amino monomers and vinyl-functional monomers:

1. Avoid formation of adduct by separating the tertiary amino monomer (e.g. dimethylaminoethyl(meth)acrylate) from the vinyl-functional monomer prior to polymerization.

2. Avoid formation of adduct by maintaining the at least one tertiary amino-containing monomer and the at least one vinyl-functional monomer water-free prior to the copolymerizing.

3. Conduct polymerization at a high temperature (typically about 70 to about 90°C, preferably about 80 to about 90°C) and at a suitable pH (typically about 3 to about 10, preferably about 4 to about 8, most preferably about 4 to about 6) to cause the adduct formed to be unstable and revert to monomers. Thus, monomers bound by the adduct will be liberated to copolymerize.

Typically, the at least one vinyl-functional monomer has is selected from at least one member of the group consisting of a monomer of Formula VIIa:



VIIa

wherein R<sup>16</sup> is a group which permits the vinyl-functional monomer to undergo Michael addition.

Preferably, the acid reactants, e.g., mineral acid (for example sulfuric acid) or citric acid, is fed to the reactor before the monomers. Typically these processes are performed as semi-batch processes. However, batch or continuous processes are not precluded.

In a particular embodiment, a tertiary amino-containing monomer, water, and an acid may be mixed in a reactor to form a neutralized tertiary amino-containing monomer mixture having a pH of about 3 to about 10. The neutralized tertiary amino-containing monomer mixture, a vinyl-functional monomer, water, and an initiator are fed to the reactor. The initiator may be a single ingredient (typically sodium persulfate) or a redox system combining an oxidizing component (typically sodium persulfate) and a reducing component (typically sodium metabisulfite). Water is typically fed directly to the reactor

with the vinyl-functional monomer and neutralized tertiary amino-containing monomer, and/or with other ingredients.

Generally, the neutralized tertiary amino-containing monomer mixture, a vinyl-functional monomer/water mixture, and initiator are separately fed to the reactor. Preferably, the neutralized tertiary amino-containing monomer mixture, the vinyl-functional monomer/water mixture, at least a portion of the initiator are separately, yet simultaneously, fed to the reactor to form the polymerization mixture. The initiator can be a single organic or inorganic compound or a redox (reduction/oxidation) system of two or more compounds. For example, United States patent no. 5,863,526, incorporated herein by reference in its entirety, discloses typical initiator systems. The polymerization mixture is maintained in the reactor at polymerization conditions including a pH of about 3 to about 10, preferably about 4 to about 8, most preferably about 4 to about 6, and a temperature of about 70 to about 90°C, preferably about 80 to about 90°C, for a time of about 1 to about 3 hours, to form a copolymer and the copolymer product is recovered.

In a second embodiment, water and acid are fed first to the reactor. Then, water-free tertiary amino-containing monomer, water-free vinyl-functional monomer and initiator are separately fed to the reactor to admix with the acid and water in the reactor. In the reactor, the monomers polymerize in the presence of the initiator described above.

Generally, the water is provided with acid and initiator. The polymerization mixture is maintained at the above-described polymerization conditions to form the copolymer product. Then the copolymer product is recovered. If desired, the tertiary amino-containing monomer, the vinyl-functional monomer, and the initiator are separately, yet simultaneously fed to the reactor.

In a third embodiment the process may be the same as the second embodiment except that the water-free monomers are mixed to form a water-free mixture prior to being fed to the reactor.

#### **METHODS OF USE**

The present invention relates to a method for providing increased suds volume and increased suds retention in suds-forming and/or foam-forming compositions, such as

personal care compositions (i.e., shampoos, hand washing compositions, body washing composition, hair removal compositions, etc.), laundry detergent compositions, especially laundry bars and/or high suds phosphate laundry compositions, hard surface cleaning compositions, agrochemical foaming compositions, oil-field foaming compositions and/or fire-firefighting foaming compositions.

In one aspect, a method for providing increased suds volume and increased suds retention while washing parts of a person's body, such as hair, hands, other parts of the body, in need of cleaning, comprising the step of contacting said parts with an aqueous solution of a personal care composition, said personal care composition comprising:

- a) an effective amount of a zwitterionic polymeric suds stabilizer as hereinbefore defined;
- b) an effective amount of a deterative surfactant; and
- c) balance carriers and other adjunct ingredients;

provided that the pH of a 10% aqueous solution of said personal care composition is from about 4 to about 12, is provided.

In another aspect, a method for providing increased suds volume and increased suds retention while washing, preferably by hand, a fabric and/or garment in need of cleaning, comprising the step of contacting said fabric and/or garment with an aqueous solution of a laundry detergent composition, said laundry detergent composition comprising:

- a) an effective amount of a zwitterionic polymeric suds stabilizer as hereinbefore defined;
- b) an effective amount of a deterative surfactant; and
- c) balance carriers and other adjunct ingredients;

provided that the pH of a 10% aqueous solution of said laundry detergent composition is from about 4 to about 12, is provided.

In yet another aspect, a method for providing increased suds volume and increased suds retention while cleaning a hard surface, such as a countertop, tile floors, bathroom fixtures, bathtubs, showers, toilets, etc., in need of cleaning, comprising the step of contacting said hard surface with an aqueous solution of a hard surface cleaning composition, said hard surface cleaning composition comprising:

- a) an effective amount of a zwitterionic polymeric suds stabilizer as hereinbefore defined;
- b) an effective amount of a deterative surfactant; and
- c) balance carriers and other adjunct ingredients;

provided that the pH of a 10% aqueous solution of said hard surface cleaning

composition is from about 4 to about 12, is provided.

In still yet another aspect, a method for providing increased suds volume and increased suds retention while treating a plant and/or crop in need of treatment, comprising the step of contacting said plant and/or crop with an aqueous solution of a agrochemical foaming composition, said agrochemical foam composition comprising:

- a) an effective amount of a zwitterionic polymeric suds stabilizer as hereinbefore defined;
- b) an effective amount of a deterative surfactant; and
- c) balance carriers and other adjunct ingredients;

provided that the pH of a 10% aqueous solution of said agrochemical foaming composition is from about 4 to about 12, is provided.

In still yet another aspect, a method for providing increased suds volume and increased suds retention while drilling for oil in oil-fields, comprising the step of contacting said drilling equipment and/or subterranean formations with an aqueous solution of a oil-field foaming composition, said oil-field foaming composition comprising:

- a) an effective amount of a zwitterionic polymeric suds stabilizer as hereinbefore defined;
- b) an effective amount of a clay; and
- c) balance carriers and other adjunct ingredients;

provided that the pH of a 10% aqueous solution of said oil-field foaming composition is from about 4 to about 12, is provided.

In still yet another aspect, a method for providing increased suds volume and increased suds retention while fighting a fire, comprising the step of contacting said fire with an aqueous solution of a fire-fighting foaming composition, said fire-fighting foaming composition comprising:

- a) an effective amount of a zwitterionic polymeric suds stabilizer as hereinbefore defined;
- b) an effective amount of a deterative surfactant; and
- c) balance carriers and other adjunct ingredients;

provided that the pH of a 10% aqueous solution of said fire-fighting foaming composition is from about 4 to about 12, is provided.

### **COMPOSITIONS FOR PERSONAL CARE PRODUCTS**

#### **Shampoos and Hand and/or Body Wash**

In addition to the zwitterionic polymeric suds stabilizers of the present invention,



beauty care and personal care products, such as shampoos and soaps for hand and/or body wash, of the present invention contain adjunct ingredients. Additional background on such products is provided by PCT application serial number PCT/US98/04474, filed March 6, 1998 and published as WO 98/38973.

5 Pearlescent additives, also known as pearlizing agents, are added to beauty and personal care products such as hair and skin care products to provide a pearly appearance to the products. Chemicals which are tiny (micron size) needles or platelets often exhibit this pearly appearance. Materials which exhibit this effect are ethylene glycol mono- and di-stearate, TiO<sub>2</sub> coated mica, bismuth oxychloride, and natural mother of pearl. Many organic  
10 materials exhibit this pearly appearance provided they can be produced in an appropriate needle or platelet shape. Ethylene glycol distearate (EGDS) or ethylene glycol monostearate (EGMS) are the most commonly utilized pearlizing agents.

A stable, mild free flowing cold pearlizing concentrate is typically prepared using  
15 i) a pearlizing agent of this invention, preferably a glycol stearate; ii) a nonionic surfactant; iii) an amphoteric surfactant emulsifier and stabilizer, iv) a glycol emulsifier and v) water; to obviate the use of cocodiethanolamide and provide excellent compatibility with any ionic surfactant. The concentrate will typically be essentially free of anionic surfactants such that the concentrate is compatible with essentially any ionic surfactants that may be used in the personal care product to which this concentrate is  
20 added.

The pearlizing agent comprises from about 5% to about 40%, preferably from about 10% to about 30% and most preferably from about 15% to about 25%, by weight based on the total weight of the concentrate.

The pearlizing agent can be selected from the group consisting of hydroxyl  
25 stearate, polyethylene glycol mono- and di-stearates, ethylene glycol mono- and distearates, stearic monoethanolamide, and mixtures thereof. The preferred agents are polyethylene glycol mono- and distearates, and ethylene glycol mono- and di-stearates. The most preferred pearlizing agents for use are: ethylene glycol mono- and di-stearates.

The fatty acid based member must be derived from a fatty acid feedstock (which  
30 includes free fatty acids, carboxylate salts, fatty mono-, di- and/or tri-glycerides) which consists of at least about 90% by weight of octadecanoic acid, i.e. the saturated fatty acid having one carboxyl group (or derivative thereof) and a seventeen carbon alkyl tail covalently bonded thereto. Stearic acid is available commercially in different grades, typically containing at least some portion of palmitic acid, i.e. the saturated fatty acid having  
35 one carboxyl group, and a fifteen carbon alkyl tail covalently bonded thereto. For example, stearic acid is available in grades of 37.5% (nominal) and 42.5% (nominal) purity. Thus,

those grades of stearic acid wherein less than about 90% of the fatty acid chains are octadecanoic acid will not be useful in making the fatty acid based member used herein, unless the stearic acid is first purified to remove a sufficient number of species which are not derived from octadecanoic acid. A useful grade of stearic acid is the 95% (nominal) grade the CTFA specifications of which are 92.5% to 97.5% stearic acid and a maximum of 5% palmitic acid. A fatty acid comprised of 90% stearic acid and 10% palmitic acid should also be useful.

The pearlizing agent is most useful as a concentrate with other components, e.g. those other components as described in published Patent Cooperation Treaty Application No. WO 98/38973, published on September 11, 1998, the disclosure of which is incorporated herein by reference.

A second component of the beauty and personal care product is a nonionic surfactant. This surfactant can function as an emulsifier and stabilizer in the formulation. The term "nonionic surfactant" as utilized herein encompasses mixtures of nonionic surfactants.

Examples of useful nonionic surfactants include condensates of ethylene oxide with a hydrophobic moiety which has an average hydrophilic lipophilic balance (HLB) between about 8 to about 16, and more preferably, between about 10 and about 12.5. These surfactants include the condensation products of primary or secondary aliphatic alcohols having from about 8 to about 24 carbon atoms, in either straight or branched chain configuration, with from about 2 to about 40, and preferably between about 2 and about 9 moles of ethylene oxide per mole of alcohol.

In a preferred embodiment the aliphatic alcohol comprises between about 9 and about 18 carbon atoms and is ethoxylated with between about 3 and about 12 moles of ethylene oxide per mole of aliphatic alcohol. Especially preferred are the about 12 to about 15 carbon primary alcohol ethoxylates containing about 5 to about 9 moles of ethylene oxide per mole of alcohol. One such material is commercially sold under the trade name NEODOL 25-9 by Shell Chemical Company. Other commercial nonionic surfactants include NEODOL 25-6.5 and NEODOL 25-7 sold by Shell Chemical Company.

Other suitable nonionic surfactants include the condensation products of about 6 to about 12 carbon atom alkyl phenols with about 3 to about 30, and preferably between about 5 and 14 moles of ethylene oxide. Examples of such surfactants are sold under the trade names Igepal CO 530, Igepal CO 630, Igepal CO720 and Igepal CO 730 by Rhone-Poulenc Inc. Still other suitable nonionic surfactants are described in U.S. Patent No. 3,976,586. To the extent necessary, this patent is expressly incorporated by reference. Most preferred

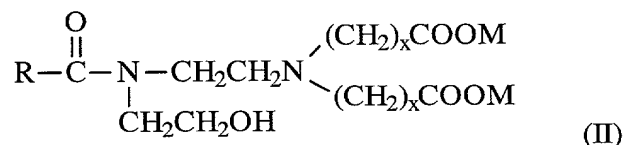
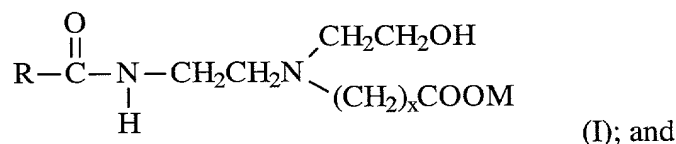
for use are mixed linear alcohol ethoxylates such as Laureth-7 sold as Rhodasurf L-790 by Rhône-Poulenc Inc.

The nonionic surfactant is incorporated in the cold pearling concentrate in an amount of from about 3% to about 30%; preferably from about 8% to about 25% and most preferably from about 10% to 20%, based on the total weight of the concentrate.

An amphoteric surfactant comprises the third component of the present invention. The term "amphoteric surfactant" as utilized herein encompasses one or more amphoteric surfactants such as mixtures of amphoteric surfactants. Preferably, amphoteric surfactants known as the betaines, their derivatives, and mixtures thereof are incorporated to provide an enhanced pearling effect.

Examples of suitable amphoteric surfactants include the alkali metal, alkaline earth metal, ammonium or substituted ammonium salts of alkyl amphocarboxy glycines and alkyl amphocarboxypropionates, alkyl amphodipropionates, alkyl amphodiacetates, alkyl amphoglycines and alkyl amphopropionates wherein alkyl represents an alkyl group having 6 to 20 carbon atoms. Other suitable amphoteric surfactants include alkyl iminopropionates, alkyl iminodipropionates and alkyl amphopropylsulfonates having between 12 and 18 carbon atoms; alkyl betaines and amidopropyl betaines and alkyl sultaines and alkylamidopropylhydroxy sultaines wherein alkyl represents an alkyl group having 6 to 20 carbon atoms.

Particularly useful amphoteric surfactants include both mono and dicarboxylates such as those of the formulae:



wherein R is an alkyl group of 6-20 carbon atoms, x is 1 or 2 and M is hydrogen or sodium. Mixtures of the above structures are particularly preferred.

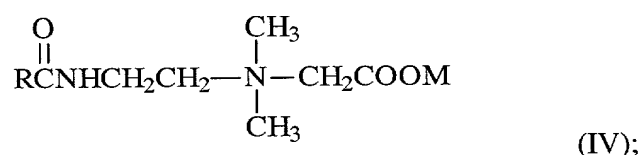
Other formulae for the above amphoteric surfactants include the following:

**Alkyl betaines**



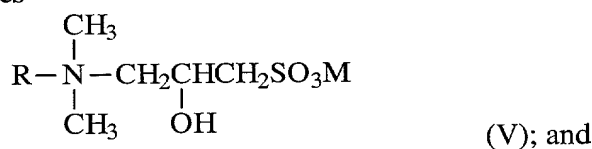
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**Amidopropyl betaines**



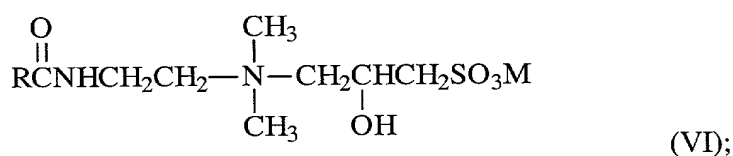
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**Alkyl sultaines**



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**Alkyl amidopropylhydroxy sultaines**



20 where R is a alkyl group of 6-20 carbon atoms and M is potassium, sodium or a monovalent cation.

Of the above amphoteric surfactants, particularly preferred are the alkali salts of alkyl amphodipropionates, alkyl amphodiacetates, alkyl amphoglycinates, alkyl amphopropyl sulfonates and alkyl amphopropionates wherein alkyl represents an alkyl group having 6 to 20 carbon atoms. Even more preferred are compounds wherein the  
25 alkyl group is derived from coconut oil or is a lauryl group, for example cocoamphodipropionate. Such cocoamphodipropionate surfactants are commercially sold

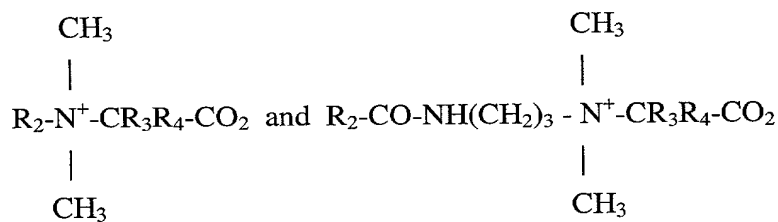
under the trademarks MIRANOL C2M-SF CONC. and MIRANOL FBS by Rhone-Poulenc Inc.

Other commercially useful amphoteric surfactants include:

- cocoamphoacetate (sold under the trademarks MIRANOL ULTRA C-32 and MIRAPON FA),
- cocoamphopropionate (sold under the trademarks MIRANOL CMSF CONC. and MIRAPON FAS),
- cocoamphodiacetate (sold under the trademarks MIRANOL C2M CONC. and MIRAPON FB),
- lauroamphoacetate (sold under the trademarks MIRANOL HM CONC. and MIRAPON LA),
- lauroamphodiacetate (sold under the trademarks MIRANOL H2M CONC. and MIRAPON LB),
- lauroamphodipropionate (sold under the trademarks MIRANOL H2M-SF CONC. AND MIRAPON LBS),
- lauroamphodiacetate obtained from a mixture of lauric and myristic acids (sold under the trademark MIRANOL BM CONC.), and
- cocoamphopropyl sulfonate (sold under the trademark MIRANOL CS CONC.)
- caproamphodiacetate (sold under the trademark MIRANOL S2M CONC.),
- caproamphoacetate (sold under the trademark MIRANOL SM CONC.),
- caproamphodipropionate (sold under the trademark MIRANOL S2M-SF CONC.), and
- stearoamphoacetate (sold under the trademark MIRANOL DM).

The most preferred amphoteric surfactant for use is cocoamphoacetate. It can be present from 0% to 10% based on the total weight of the concentrate. Preferably, cocoamphoacetate will comprise from about 1% to about 7% and most preferably from about 2% to about 4% of the concentrate.

Also useful herein are the betaines and amidobetaines which are compounds of the general structure:



respectively wherein R<sub>2</sub> is C<sub>8</sub> - C<sub>22</sub> alkyl or alkenyl; R<sub>3</sub> is H or C<sub>1</sub> - C<sub>4</sub> alkyl; and R<sub>4</sub> is H or C<sub>1</sub> - C<sub>4</sub> alkyl.

The betaines useful herein include the high alkyl betaines such as cocodimethyl carboxymethyl betaine, lauryl dimethyl carboxymethyl betaine, lauryl dimethyl alpha-carboxy-ethyl betaine, cetyl dimethyl carboxymethyl betaine, lauryl bis-(2-hydroxy-ethyl)carboxy methyl betaine, stearyl bis-(2-hydroxy-propyl)carboxymethyl betaine, oleyl dimethyl gamma-carboxypropyl betaine, and lauryl bis-(2-hydroxypropyl)alpha-carboxyethyl betaine. The sulfobetaines are also preferred and may be represented by cocodimethyl sulfopropyl betaine, stearyldimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, lauryl bis-(2-hydroxy-ethyl)sulfopropyl betaine and mixtures thereof. A particularly preferred composition utilizes cocoamidopropyl betaine.

Most preferably, the amphoteric surfactant can be cocoamphoacetate and cocoamidopropyl betaine acting as amphoteric co-emulsifiers.

The amphoteric surfactant can be present from about 2% to about 20% weight percent based on the total weight of the pearlizing concentrate. Preferably, the amphoteric will comprise from about 4% to about 16%, most preferably from about 6% to about 10%, of the pearlizing concentrate.

The fourth component consists of a glycol emulsifier. Propylene glycol (1,2, and 1, 3) and other alcohols such as 1, 3 - butylene glycol, 2, 3 - butylene glycol, ethylene glycol and mixtures thereof are useful emulsifiers. The glycol emulsifier can be present from 0% to about 15%, preferably from about 1% to about 10% and most preferably from about 2% to about 5%.

For the fifth component, the remainder is water, preferably deionized. Generally, water is added in an amount of from about 20% to about 70%, preferably from about 30% to about 60%, and most preferably from about 40% to about 55% based on the total weight of the concentrate.

Non-essential optional components can be utilized in the concentrates of the present invention as a convenient means of incorporation into beauty and personal care products. Such conventional optional ingredients are well known to those skilled in the art, e.g., preservatives such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; thickeners and viscosity modifiers such as block polymers of ethylene oxide and propylene oxide, e.g. ANTAROX F-88 (Rhone-Poulenc Inc.), sodium chloride, sodium sulfate, polyvinyl alcohol, and ethyl alcohol; pH adjusting agents such as citric acid, succinic acid, phosphoric acid, sodium hydroxide, sodium carbonate; perfumes; dyes; and sequestering agents such as disodium ethylenediamine tetra-acetate.

Such agents generally are used individually at levels of from 0% to about 2%, preferably from 0.01% to about 1.0% by weight of the concentrate.

The pH of the concentrate compositions is not critical and can be in the range of from about 2 to about 12, preferably from about 4 to about 10 and most preferably from about 6 to about 8. The pH can be adjusted using a buffer such as citric acid.

The order of addition to the mixing tank of the individual components of the concentrate is not critical nor is the reasonably elevated temperature; however, preferably the water and pearlizing agent are intimately blended at from about 50° to about 90°C, more preferably from about 70° to about 80°C with high agitation until the pearlizing agent is emulsified. The nonionic and amphoteric surfactants are then blended into the mix until the mixture is clear. The mixture is then allowed to cool to room temperature. Generally, the concentrate can be stored at a temperature of from about 0°C to about 45°C, preferably from about 15°C to about 35°C for at least one day and preferably two days in order to fully develop its pearlizing characteristics.

The personal care compositions may further comprise a silicone compound. As referred to herein, a silicone compound is a nonfunctionalized siloxane having a viscosity of from about 5 to about 600,000 cs (centistoke), and preferably from about 350 to about 10,000 cs, at 25° C. The so-called "rigid silicones", as described in U.S. Pat. No. 4,902,499, herein incorporated by reference, having a viscosity above 600,000 cs at 20° C, e.g., 700,000 cs plus, and a weight average molecular weight of at least about 500,000, also are useful. The silicone compound is typically a polydimethylsiloxane, typically a linear polydimethylsiloxane terminated at each end with a trimethylsilyl group. The silicone compound can be a dimethicone as specified by the CTFA, i.e. an alpha,omega-trimethylsilyl-polydimethylsiloxane having a viscosity at 25°C of at least 25 centistokes and less than 60,000 centistokes. The silicone compound is typically used in the context of a shampoo and is added to the composition in an amount sufficient to impart improved combing and improved feel, such as softness, to the hair after shampooing.

The silicone hair conditioning agent for use herein will preferably have viscosity of from about 1,000 to about 2,000,000 centistokes at 25o C., more preferably from about 10,000 to about 1,800,000, even more preferably from about 100,000 to about 1,500,000. The viscosity can be measured by means of a glass capillary viscometer as set forth in Dow Corning Corporate Test Method CTM0004, Jul. 20, 1970.

The silicone hair conditioning agent will be used in the shampoo compositions hereof at levels of from about 0.1% to about 10% by weight of the composition, preferably from about 0.5% to about 8%, more preferably from about 1% to about 5%.

Suitable insoluble, nonvolatile silicone fluids include polyalkyl siloxanes, polyaryl siloxanes, polyalkylaryl siloxanes, polyether siloxane copolymer and mixtures thereof. However, other insoluble, nonvolatile silicone fluids having hair conditioning properties may be used. The term "nonvolatile" as used herein shall mean that the silicone material exhibits very low or no significant vapor pressure at ambient conditions, as is well understood in the art. The term "silicone fluid" shall mean flowable silicone materials having a viscosity of less than 1,000,000 centistokes at 25° C. Generally, the viscosity of the fluid will be between about 5 and 1,000,000 centistokes at 25° C., preferably between about 10 and about 100,000. The term "silicone", as used herein, shall be synonymous with the term "polysiloxane".

The nonvolatile polyalkylsiloxane fluids that may be used include, for example, polydimethyl siloxanes. These siloxanes are available, for example, from the General Electric Company as a VISCASIL series and from Dow Corning as the Dow Corning 200 series.

The polyalkylaryl siloxane fluids that may be used, also include, for example, polymethylphenylsiloxanes. These siloxanes are available, for example, from the General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid.

The polyether siloxane copolymers that may be used include, for example, a polypropylene oxide modified dimethylpolysiloxane (e.g., Dow Corning DC-1248) although ethylene oxide or mixtures of ethylene oxide and propylene oxide may also be used. The ethylene oxide and polypropylene oxide level must be sufficiently low to prevent solubility in water and the composition hereof.

Silicone fluids hereof also include polyalkyl or polyaryl siloxanes with the structure shown in U.S. Patent No. 5,573,709, the disclosure of which is incorporated herein by reference., herein R is alkyl or aryl, and x is an integer from about 7 to about 8,000 may be used. "A" represents groups which block the ends of the silicone chains.

The alkyl or aryl groups substituted on the siloxane chain (R) or at the ends of the siloxane chains (A) may have any structure as long as the resulting silicones remain fluid at room temperature, are hydrophobic, are neither irritating, toxic nor otherwise harmful when applied to the hair, are compatible with the other components of the composition, are chemically stable under normal use and storage conditions, and are capable of being deposited on and of conditioning hair.

Suitable A groups include methyl, methoxy, ethoxy, propoxy, and aryloxy. The two R groups on the silicone atom may represent the same group or different groups. Preferably, the two R groups represent the same group. Suitable R groups include methyl,



ethyl, propyl, phenyl, methylphenyl and phenylmethyl. The preferred silicones are polydimethyl siloxane, polydiethylsiloxane, and polymethylphenylsiloxane. Polydimethylsiloxane is especially preferred.

References disclosing suitable silicone fluids include U.S. Pat. No. 2,826,551, 5 Geen; U.S. Pat. No. 3,964,500, Drakoff, issued Jun. 22, 1976; U.S. Pat. No. 4,364,837, Pader; and British Patent 849,433, Woolston. All of these patents are incorporated herein by reference. Also incorporated herein by reference is Silicon Compounds distributed by Petrarch Systems, Inc., 1984. This reference provides an extensive (though not exclusive) listing of suitable silicone fluids.

10 Another silicone material that can be especially useful in the silicone conditioning agents is insoluble silicone gum. The term "silicone gum", as used herein, means polyorganosiloxane materials having a viscosity at 25° C. of greater than or equal to 1,000,000 centistokes. Silicone gums are described by Petrarch and others including U.S. Pat. No. 4,152,416, Spitzer et al., issued May 1, 1979 and Noll, Walter, Chemistry and 15 Technology of Silicones, New York: Academic Press 1968. Also describing silicone gums are General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76. All of these described references are incorporated herein by reference. The "silicone gums" will typically have a mass molecular weight in excess of about 200,000, generally between about 200,000 and about 1,000,000. Specific examples include 20 polydimethylsiloxane, (polydimethylsiloxane) (methylvinylsiloxane) copolymer, poly(dimethylsiloxane) (diphenyl siloxane)(methylvinylsiloxane) copolymer and mixtures thereof.

Preferably the silicone hair conditioning agent comprises a mixture of a polydimethylsiloxane gum, having a viscosity greater than about 1,000,000 centistokes 25 and polydimethylsiloxane fluid having a viscosity of from about 10 centistokes to about 100,000 centistokes, wherein the ratio of gum to fluid is from about 30:70 to about 70:30, preferably from about 40:60 to about 60:40.

Another optional ingredient that can be included in the silicone conditioning agent is silicone resin. Silicone resins are highly crosslinked polymeric siloxane systems. The 30 crosslinking is introduced through the incorporation of trifunctional and tetrafunctional silanes with monofunctional or difunctional, or both, monomer units during manufacture of the silicone resin. As is well understood in the art, the degree of crosslinking that is required in order to result in a silicone resin will vary according to the specific silane units incorporated into the silicone resin. In general, silicone materials which have a sufficient 35 level of trifunctional and tetrafunctional siloxane monomer units (and hence, a sufficient level of crosslinking) such that they dry down to a rigid, or hard, film are considered to be

silicone resins. The ratio of oxygen atoms to silicon atoms is indicative of the level of crosslinking in a particular silicone material. Silicone materials which have at least about 1.1 oxygen atoms per silicon atom will generally be silicone resins herein. Preferably, the ratio of oxygen:silicon atoms is at least about 1.2:1.0. Silanes used in the manufacture of silicone resins include monomethyl-, dimethyl-, monophenyl-, diphenyl-, methylphenyl-, monovinyl-, and and methylvinyl-chlorosilanes, and tetra-chlorosilane, with the methyl-substituted silanes being most commonly utilized. Preferred resins are offered by General Electric as GE SS4230 and SS4267. Commercially available silicone resins will generally be supplied in an unhardened form in a low viscosity volatile or nonvolatile silicone fluid.

10 The silicone resins for use herein should be supplied and incorporated into the present compositions in such unhardened form, as will be readily apparent to those skilled in the art.

Background material on silicones including sections discussing silicone fluids, gums, and resins, as well as manufacture of silicones, can be found in Encyclopedia of Polymer Science and Engineering, Volume 15, Second Edition, pp 204-308, John Wiley & Sons, Inc., 1989, incorporated herein by reference.

Silicone materials and silicone resins in particular, can conveniently be identified according to a shorthand nomenclature system well known to those skilled in the art as "MDTQ" nomenclature. Under this system, the silicone is described according to presence of various siloxane monomer units which make up the silicone. Briefly, the symbol M denotes the monofunctional unit  $(\text{CH}_3)_3\text{SiO}_{0.5}$ ; D denotes the difunctional unit  $(\text{CH}_3)_2\text{SiO}$ ; T denotes the trifunctional unit  $(\text{CH}_3)\text{SiO}_{1.5}$ ; and Q denotes the quadri- or tetra-functional unit  $\text{SiO}_2$ . Primes of the unit symbols, e.g., M', D', T', and Q' denote substituents other than methyl, and must be specifically defined for each occurrence.

25 Typical alternate substituents include groups such as vinyl, phenyls, amines, hydroxyls, etc. The molar ratios of the various units, either in terms of subscripts to the symbols indicating the total number of each type of unit in the silicone (or an average thereof) or as specifically indicated ratios in combination with molecular weight complete the description of the silicone material under the MDTQ system. Higher relative molar amounts of T, Q, T' and/or Q' to D, D', M and/or or M' in a silicone resin is indicative of higher levels of crosslinking. As discussed before, however, the overall level of crosslinking can also be indicated by the oxygen to silicon ratio.

The silicone resins for use herein which are preferred are MQ, MT, MTQ, MQ and MDTQ resins. Thus, the preferred silicone substituent is methyl. Especially preferred are MQ resins wherein the M:Q ratio is from about 0.5:1.0 to about 1.5:1.0 and the average molecular weight of the resin is from about 1000 to about 10,000.

The weight ratio of the nonvolatile silicone fluid component to the silicone resin component is from about 4:1 to about 400:1, preferably this ratio is from about 9:1 to about 200:1, more preferably from about 19:1 to about 100:1, particularly when the silicone fluid component is a polydimethylsiloxane fluid or a mixture of polydimethylsiloxane fluid and polydimethylsiloxane gum as described above.

The shampoo will contain a deterative surfactant. These include anionic, cationic, nonionic surfactants, amphoteric surfactants, zwitterionic surfactants. Examples of anionic surfactants are described in U.S. Patent No. 5,573,709, the entire disclosure of which is incorporated by reference. However, the shampoo will typically be essentially free of anionic surfactants, e.g. contain less than 0.5% by weight of species that can properly be characterized as anionic surfactants. If the formulation does not include an anionic surfactant, cationic deterative surfactants can also be used.

Nonionic deterative surfactants which can be used include those broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. Examples of preferred classes of nonionic deterative surfactants are:

1. The polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 20 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to from about 10 to about 60 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octane, or nonane, for example.

2. Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products which may be varied in composition depending upon the balance between the hydrophobic and hydrophilic elements which is desired. For example, compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5,000 to about 11,000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of about 2,500 to about 3,000, are satisfactory.

3. The condensation product of aliphatic alcohols having from about 8 to about 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from about 10 to

about 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction havin from about 10 to about 14 carbon atoms.

4. Long chain tertiary amine oxides corresponding to the following general formula:



wherein R<sup>1</sup> contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to about 1 glyceryl moiety, and R<sup>2</sup> and R<sup>3</sup> contain from about 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals. The arrow in the formula is a conventional representation of a semipolar bond. Examples of amine oxides suitable for use in this invention include dimethyldodecylamine oxide, oleyldi(2-hydroxyethyl) amine oxide, dimethyloctylamine oxide, dimethyl-decylamine oxide, dimethyl-tetradecylamine oxide, 3,6,9-trioxaheptadecyldiethylamine oxide, di(2hydroxyethyl)-tetradecylamine oxide, 2-dodecoxyethyl dimethylamine oxide, 3-dodecoxy-2-hydroxypropyldi(3-hydroxypropyl) amine oxide, dimethylhexadecylamine oxide.

5. Long chain tertiary phosphine oxides corresponding to the following general formula:



wherein R contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from about 8 to about 18 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety and R' and R'' are each alkyl or monohydroxyalkyl groups containing from about 1 to about 3 carbon atoms. The arrow in the formula is a conventional representation of a semipolar bond. Examples of suitable phosphine oxides are: dodecyldimethylphosphine oxide, tetradecyldimethylphosphine oxide, tetradecylmethylethylphosphine oxide. 3,6,9,-trioxaoctadecyldimethylphosphine oxide, cetyldimethylphosphine oxide, 3-dodecoxy-2-hydroxypropyldi (2-hydroxyethyl) phosphine oxide, stearyldimethylphosphine oxide, cetylethylpropylphosphine oxide, oleyldiethylphosphine oxide, dodecyldiethylphosphine oxide, tetradecyldiethylphosphine oxide, dodecyldipropylphosphine oxide, dodecyldi(hydroxymethyl)phosphine oxide, dodecyldi(2-hydroxyethyl)phosphine oxide, tetradecylmethyl-2-hydroxypropylphosphine oxide, oleyldimethylphosphine oxide, 2-hydroxydodecyldimethylphosphine oxide.

6. Long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of from about 1 to about 3 carbon atoms (usually methyl) and one long hydrophobic chain which include alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 8 to about 20 carbon atoms, from 0 to about 10 ethylene oxide

moieties and from 0 to about 1 glyceryl moiety. Examples include: octadecyl methyl sulfoxide, 2-ketotridecyl methyl sulfoxide, 3,6,9,-trixaoctadecyl 2-hydroxyethyl sulfoxide, dodecyl methyl sulfoxide, oleyl 3-hydroxypropyl sulfoxide, tetradecyl methyl sulfoxide, 3-methoxytridecyl methyl sulfoxide, 3-hydroxytridecyl methyl sulfoxide, 3-hydroxy-4-dodecoxybutyl methyl sulfoxide.

Zwitterionic deterative surfactants are exemplified by those which can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight or branched chain, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is: found in U.S. Patent No. 5,573,709, which is incorporated herein by reference, wherein  $R^2$  contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms;  $R^3$  is an alkyl or monohydroxyalkyl group containing about 1 to about 3 carbon atoms; X is 1 when Y is a sulfur atom, and 2 when Y is a nitrogen or phosphorus atom;  $R^4$  is an alkylene or hydroxyalkylene of from about 1 to about 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

Examples of such surfactants include:

4-[N,N-di(2-hydroxyethyl)-N-octadecylammonio]-butane-1-carboxylate;  
5-[S-3-hydroxypropyl-S-hexadecylsulfonio]-3-hydroxypentane-1- sulfate;  
3-[P,P-diethyl-P-3,6,9-trioxatetradecylphosphonio]-2-hydroxy-propane-1-phosphate;

3-[N,N-dipropyl-N-3-dodecoxy-2-hydroxypropylammonio]-propane-1-phosphonate;

3-(N,N-dimethyl-N-hexadecylammonio)propane-1-sulfonate;  
3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1- sulfonate;  
4-[N,N-di(2-hydroxyethyl)-N-(2-hydroxydodecyl)ammonio]-butane-1-

carboxylate;  
3-[S-ethyl-S-(3-dodecoxy-2-hydroxypropyl)sulfonio]-propane-1-phosphate;  
3-[P,P-dimethyl-P-dodecylphosphonio]-propane-1-phosphonate; and  
5-[N,N-di(3-hydroxypropyl)-N-hexadecylammonio]-2-hydroxy-pentane-1-sulfate.

Other zwitterionics such as betaines can also useful in the present invention.

Examples of betaines useful herein include the high alkyl betaines, such as coco dimethyl carboxymethyl betaine, cocoamidopropyl betaine, cocobetaine, lauryl amidopropyl

betaine, oleyl betaine, lauryl dimethyl carboxymethyl betaine, lauryl dimethyl alphacarboxyethyl betaine, cetyl dimethyl carboxymethyl betaine, lauryl bis-(2-hydroxyethyl) carboxymethyl betaine, stearyl bis-(2-hydroxypropyl) carboxymethyl betaine, oleyl dimethyl gamma-carboxypropyl betaine, and lauryl bis-(2-hydroxypropyl)alpha-carboxyethyl betaine. The sulfobetaines may be represented by coco dimethyl sulfopropyl betaine, stearyl dimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, lauryl bis-(2-hydroxyethyl ) sulfopropyl betaine and the 1 like; amidobetaines and amidosulfobetaines, wherein the  $RCONH(CH_2)_3$  radical is attached to the nitrogen atom of the betaine are also useful in this invention. Preferred betaines for use in the present compositions are cocoamidopropyl betaine, cocobetaine, lauryl amidopropyl betaine, and oleyl betaine.

Examples of amphoteric deterative surfactants which can be used in the compositions of the present invention are those which are broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. Examples of compounds falling within this definition are sodium 3-dodecyl -aminopropionate, sodium 3-dodecylaminopropane sulfonate, sodium lauryl sarcosinate, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Pat. No. 2,658,072, N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Pat. No. 2,438,091, and the products sold under the trade name "MIRANOL" TM and described in U.S. Pat. No. 2,528,378. Another deterative surfactant optional for use in the compositions of the present invention is cocoamphocarboxy glycinate.

The most preferred shampoos of the present invention contain combinations of amphoteric surfactants, zwitterionic surfactants, and nonionic surfactants and are essentially free of anionic surfactants. The shampoos typically contain from about 0% to about 6% of amphoteric surfactants, about 0% to about 8% of zwitterionic surfactants, from 0% to about 14% of ethoxylated alkyl sulfates, and from about 0% to about 10% of an optional anionic surfactant surfactants, e.g. about 3% to about 7% alkyl sulfates, with a total surfactant level of from about 10% to about 25%.

The formulated shampoo and soap systems of the present invention can contain a variety of non-essential optional components suitable for rendering such compositions more acceptable. Such conventional optional ingredients are well known to those skilled in the art, e.g., preservatives such as benzyl alcohol, methyl paraben, propyl paraben and

imidazolidinyl urea; cationic surfactants such as cetyl trimethyl ammonium chloride, lauryl trimethyl ammonium chloride, tricetyl methyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride, and di(partially hydrogenated tallow) dimethyl ammonium chloride; thickeners and viscosity modifiers such as block polymers of ethylene oxide and propylene oxide, e.g. ANTAROX F-88 (Rhone-Poulenc Inc.), sodium chloride, sodium sulfate, polyvinyl alcohol, and ethyl alcohol; pH adjusting agents such as citric acid, succinic acid, phosphoric acid, sodium hydroxide, sodium carbonate; perfumes; dyes; and sequestering agents such as disodium ethylenediamine tetra-acetate. Such agents generally are used individually at levels of from about 0.01% to about 10%, preferably from 0.5% to about 5.0% by weight of the composition.

Shampoos may also include antidandruff agents such as pyrithione salts, preferably zinc pyrithione, as disclosed by PCT application number PCT/US98/04139, filed March 4, 1998 and published as WO 98/41505, incorporated herein by reference in its entirety.

#### Hair Removal Personal Care Products

The zwitterionic polymeric suds stabilizer (foam enhancer) of the present invention may also be employed with foam forming shaving gels and shaving creams. Typical foaming shaving gels are disclosed by U.S. Patent Nos. 5,902,778 to Hartmann, et al; 5,858,343 to Szymczak; and 5,853,710 to Dehan, et al, all of which are incorporated herein by reference in their entirety. Typical foam shaving creams are disclosed by U.S. Patent Nos. 5,686,024 to Dahanayake, et al; 5,415,860 to Beucherie, et al; 5,902,574 to Stoner, et al; and 5,104,643 to Grollier, et al, all of which are incorporated herein by reference in their entirety.

The foam enhancer is also useful in a foam dephilatory. An example of a foam dephilatory is disclosed in U.S. Patent No. 4,734,099 to Cyprien.

#### COMPOSITIONS AND METHODS OF USE FOR LAUNDRY DETERGENTS

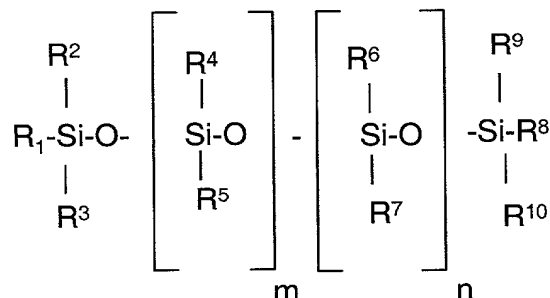
In addition to the zwitterionic polymeric suds stabilizers of the present invention used as soil release agents, laundry detergents of the present invention further include adjunct ingredients. A variety of such adjunct laundry detergent ingredients are disclosed by PCT International Publication No. WO 98/39401, incorporated herein by reference in its entirety.

In general, the laundry detergent compositions are solid granules, liquid or gel and comprise a major amount by weight of detergent and a minor amount of the soil release polymer of the present invention. Also, in general the method for washing fabric of the present invention comprises washing a fabric article in a washing medium comprised of a major amount by weight of water and a first minor amount by weight of detergent and a

second minor amount by weight of the soil release polymer. Minor amounts of adjunct components may also be present.

I. Aminoalkyl/alkoxysilane-silicone Compounds

One of the adjunct components of the compositions and methods of this invention  
5 is an aminosilicone compound, typically an aminosilicone compound of the formula:



wherein:

10  $\text{R}^1$  and  $\text{R}^8$  are independently selected from the group consisting of hydrogen, hydroxyl, alkyl (typically  $\text{C}_1\text{-C}_4$ ) and alkoxy (typically  $\text{C}_1\text{-C}_4$ ),

$\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^9$ , and  $\text{R}^{10}$  are independently selected from the group consisting of alkyl (typically  $\text{C}_1\text{-C}_4$ ) and alkoxy (typically  $\text{C}_1\text{-C}_4$ ), provided that one of  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^9$ , and  $\text{R}^{10}$  may be selected from the group consisting of a primary amino-substituted alkyl group,  
15 and a secondary amino-substituted alkyl group (typically an N-(amino-alkyl)-substituted aminoalkyl group such that the compound will have both primary and secondary amine functionality),

$\text{R}^4$ ,  $\text{R}^5$ , and  $\text{R}^6$  are independently selected from the group consisting of alkyl (typically  $\text{C}_1\text{-C}_4$ ) and aryl (typically phenyl),

20  $\text{R}^7$  is selected from the group consisting of a primary amino-substituted alkyl group, and a secondary amino-substituted alkyl group (typically an N-(aminoalkyl)-substituted aminoalkyl group such that the compound will have both primary and secondary amine functionality),

m and n are numbers wherein m is greater than n (typically the ratio of m:n is from  
25 about 2:1 to about 500:1, more typically from about 40:1 to about 300:1 and most typically from about 85:1 to about 185:1) and the sum of n and m yield an aminosilicone compound with a viscosity of about 10 to about 100,000 cps at  $25^\circ$  (typically the sum of n and m is from about 5 to about 600, more typically from about 50 to about 400 and most typically from about 135 to about 275).



The preparation and properties of silicone compounds is discussed generally in Silicones: Chemistry and Technology, pp. 21-31 and 75-90 (CRC Press, Vulkan- Verlag, Essen, Germany, 1991) and in Harman et al. "Silicones", Encyclopedia of Polymer Science and Engineering, vol. 15, pp. (John Wiley & Sons, Inc. 1989), the disclosures of which are incorporated herein by reference. Preferred aminosilicone compounds are disclosed, for example in JP-047547 (J57161170) (Shinetsu Chem. Ind. KK). Particularly preferred aminosilicone compounds are the three of formula I wherein (1)  $R^1$  and  $R^8$  are methoxy,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^9$ , and  $R^{10}$  are methyl,  $R^7$  is N-aminoethyl-3-aminopropyl, m is about 135, and n is about 1.5, (2)  $R^1$  and  $R^8$  are methoxy,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^9$ , and  $R^{10}$  are methyl,  $R^7$  is N-aminoethyl-3-aminopropyl, m is about 270, and n is about 1.5, and (3)  $R^1$  and  $R^8$  are ethoxy,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^9$ , and  $R^{10}$  are methyl,  $R^7$  is 3-aminopropyl, m is about 135, and n is about 1.5. Other aminosilicone compounds include those wherein  $R^1$ ,  $R^2$ , and  $R^8$  are ethoxy,  $R^3$  is 3-aminopropyl,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^9$ , and  $R^{10}$  are methyl, m is about 8, and n is zero. Of course, for pure aminosilicone compounds, the numbers m and n will be integers, but for mixtures of compounds, m and n will be expressed as fractions or compound numbers which represent an average of the compounds present. Further, the formula above is not meant to imply a block copolymer structure, thus, the aminosilicone compound may have a random or block structure. Typically, at least about 50% by weight of the  $R^4$ ,  $R^5$ , and  $R^6$  groups will be methyl groups, more typically at least about 90% and even more typically about 100%.

The aminosilicone compound typically will be in the form of a liquid or viscous oil at room temperature.

The aminosilicones described below in the context of the soluble powder detergent compositions can be substituted for the aminosilicones described above.

## II. Insoluble Carriers

While the aminosilicone can be used in certain compositions and methods of this invention alone or as an aqueous emulsion, the aminosilicone is preferably used in association with a water-insoluble solid carrier, for example, clays, natural or synthetic silicates, silica, resins, waxes, starches, ground natural minerals, such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite, bentonite or diatomaceous earth, or ground synthetic minerals, such as silica, alumina, or silicates especially aluminum or magnesium silicates. Useful inorganic agents comprise those of natural or synthetic mineral origin. Specific examples of carriers include diatomaceous earths, e.g. Celite Registered TM (Johns Manville Corp., Denver, Col.) and the smectite clays such as the saponites and the montmorillonite colloidal clays such as Veegum Registered TM and Van Gel Registered TM (Vanderbilt Minerals, Murray, KY), or Magnabrite Registered

TM (American Colloid Co., Skokie, IL). Synthetic silicate carriers include the hydrous calcium silicate, Micro-Cel Registered TM and the hydrous magnesium silicate Celkate Registered TM (Seegot, Inc., Parsippany, NJ). Inosilicates carriers such as the naturally-occurring calcium meta-silicates such as wollastonite, available as the NYAD Registered  
5 TM wollastonite series (Processed Minerals Inc., Willsboro, NY) can also be mentioned. Synthetic sodium magnesium silicate clays, hectorite clays, and fumed silicas can also be mentioned as carriers. The carrier can be a very finely divided material of average particle diameter below 0.1 micron. Examples of such carriers are fumed silica and precipitated silica; these generally have a specific surface (BET) of above 40 m<sup>2</sup> /g.

10 The clays that are particularly useful elements of the compositions and methods of this invention are those which cooperate with the silicone compounds to wash laundry better than would be expected from the actions of the individual components in detergent compositions. Such clays include the montmorillonite-containing clays which have swelling properties (in water) and which are of smectite structure. Typical of the smectite  
15 clays for use in the present invention is bentonite and typically the best of the bentonites are those which have a substantial swelling capability in water, such as the sodium bentonites, the potassium bentonites, or which are swellable in the presence of sodium or potassium ions, such as calcium bentonite. Such swelling bentonites are also known as western or Wyoming bentonites, which are essentially sodium bentonite. Other  
20 bentonites, such as calcium bentonite, are normally non-swelling. Among the preferred bentonites are those of sodium and potassium, which are normally swelling, and calcium and magnesium, which are normally non-swelling, but are swellable. Of these it is preferred to utilize calcium (with a source of sodium being present) and sodium bentonites. The bentonites employed are not limited to those produced in the United  
25 States of America, such as Wyoming bentonite, but also may be obtained from Europe, including Italy and Spain, as calcium bentonite, which may be converted to sodium bentonite by treatment with sodium carbonate, or may be employed as calcium bentonite. Typically, the clay will have a high montmorillonite content and a low content of cristobalite and/or quartz. Also, other montmorillonite-containing smectite clays of  
30 properties like those of the bentonites described may be substituted in whole or in part for the bentonites described herein, but typically the clay will be a sodium bentonite with high montmorillonite content and low cristobalite and quartz contents.

The swellable bentonites and similarly operative clays are of ultimate particle sizes in the micron range, e.g., 0.01 to 20 microns and of actual particle sizes less than  
35 100 or 150 microns, such as 40 to 150 microns or 45 to 105 microns. Such size ranges also apply to the zeolite builders, which will be described later herein. The bentonite and

other such suitable swellable clays may be agglomerated to larger particle sizes too, such as up to 2 or 3 mm. in diameter.

The ratio of aminosilicone compound to carrier will typically range from about 0.001 to about 2, more typically from about 0.02 to about 0.5, and most typically from about 0.1 to about 0.3.

### III. Detergents

The methods and compositions of this laundry detergent invention all employ a detergent, and optionally, other functional ingredients. Examples of the detergents and other functional ingredients that can be used are disclosed in U.S. Serial No. 08/726,437, filed October 4, 1996, the disclosure of which is incorporated herein by reference. The detergent can be selected from a wide variety of surface active agents.

#### A. Nonionic Surfactants

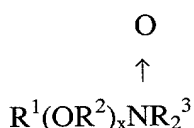
Nonionic surfactants, including those having an HLB of from 5 to 17, are well known in the detergency art. Examples of such surfactants are listed in U.S. Patent No. 3,717,630, Booth, issued February 20, 1973, and U. S. Patent No. 3,332,880, Kessler et al., issued July 25, 1967, each of which is incorporated herein by reference. Nonlimiting examples of suitable nonionic surfactants which may be used in the present invention are as follows:

- (1) The polyethylene oxide condensates of alkyl phenols. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration with ethylene oxide, said ethylene oxide being present in an amount equal to 5 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds can be derived, for example, from polymerized propylene, diisobutylene, and the like. Examples of compounds of this type include nonyl phenol condensed with about 9.5 moles of ethylene oxide per mole of nonyl phenol; dodecylphenol condensed with about 12 moles of ethylene oxide per mole of phenol; dinonyl phenol condensed with about 15 moles of ethylene oxide per mole of phenol; and diisooctyl phenol condensed with about 15 moles of ethylene oxide per mole of phenol. Commercially available nonionic surfactants of this type include Igepal CO-630, marketed by Rhone-Poulenc Inc. and Triton X-45, X-114, X-100, and X-102, all marketed by Union Carbide.

- 34

- (5) Semi-polar nonionic detergent surfactants include water-soluble amine oxides containing one alkyl moiety of from about 10 to 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of about 10 to 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to 3 carbons atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to 3 carbon atoms.

Preferred semi-polar nonionic detergent surfactants are the amine oxide detergent surfactants having the formula

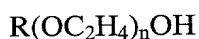


wherein  $\text{R}^1$  is an alkyl, hydroxy alkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms.  $\text{R}^2$  is an alkylene or hydroxy alkylene group containing from 2 to 3 carbon atoms or mixtures thereof,  $x$  is from 0 to about 3 and each  $\text{R}^3$  is an alkyl or hydroxy alkyl group containing from 1 to about 3 carbon atoms or a polyethylene oxide group containing from one to about 3 ethylene oxide groups and said  $\text{R}^3$  groups can be attached to each other, e.g., through an oxygen or nitrogen atom to form a ring structure.

Preferred amine oxide detergent surfactants are  $\text{C}_{10}$ - $\text{C}_{18}$  alkyl dimethyl amine oxide,  $\text{C}_8$ - $\text{C}_{18}$  alkyl dihydroxy ethyl amine oxide, and  $\text{C}_{8-12}$  alkoxy ethyl dihydroxy ethyl amine oxide.

Nonionic detergent surfactants (1)-(4) are conventional ethoxylated nonionic detergent surfactants and mixtures thereof can be used.

Preferred alcohol ethoxylate nonionic surfactants for use in the compositions of the liquid, powder, and gel applications are biodegradable and have the formula



wherein  $\text{R}$  is a primary or secondary alkyl chain of from about 8 to about 22, preferably from about 10 to about 20 carbon atoms and  $n$  is an average of from about 2 to about 12, particularly from about 2 to about 9. The nonionics have an HLB (hydrophilic-lipophilic balance) of from about 5 to about 17, preferably from about 6 to about 15. HLB is

defined in detail in Nonionic Surfactants, by M. J. Schick, Marcel Dekker, Inc., 1966, pages 606-613, incorporated herein by reference. In preferred nonionic surfactants, n is from 3 to 7. Primary linear alcohol ethoxylates (e.g., alcohol ethoxylates produced from organic alcohols which contain about 20% 2-methyl branched isomers, commercially available from Shell Chemical Company under the trademark Neodol) are preferred from a performance standpoint.

Particularly preferred nonionic surfactants for use in liquid, powder, and gel applications include the condensation product of C<sub>10</sub> alcohol with 3 moles of ethylene oxide; the condensation product of tallow alcohol with 9 moles of ethylene oxide; the condensation product of coconut alcohol with 5 moles of ethylene oxide; the condensation product of coconut alcohol with 6 moles of ethylene oxide; the condensation product of C<sub>12</sub> alcohol with 5 moles of ethylene oxide; the condensation product of C<sub>12-13</sub> alcohol with 6.5 moles of ethylene oxide, and the same condensation product which is stripped so as to remove substantially all lower ethoxylate and nonethoxylated fractions; the condensation product of C<sub>12-13</sub> alcohol with 2.3 moles of ethylene oxide, and the same condensation product which is stripped so as to remove substantially all lower ethoxylated and nonethoxylated fractions; the condensation product of C<sub>12-13</sub> alcohol with 9 moles of ethylene oxide; the condensation product of C<sub>14-15</sub> alcohol with 2.25 moles of ethylene oxide; the condensation product of C<sub>14-15</sub> alcohol with 4 moles of ethylene oxide; the condensation product of C<sub>14-15</sub> alcohol with 7 moles of ethylene oxide; and the condensation product of C<sub>14-15</sub> alcohol with 9 moles of ethylene oxide. For bar soap applications, nonionic surfactants are preferably solids at room temperature with a melting point above about 25° C., preferably above about 30° C. Bar compositions of the present invention made with lower melting nonionic surfactants are generally too soft, not meeting the bar firmness requirements of the present invention.

Also, as the level of nonionic surfactant increases, i.e., above about 20% by weight of the surfactant, the bar can generally become oily.

Examples of nonionic surfactants usable herein, but not limited to bar applications, include fatty acid glycerine and polyglycerine esters, sorbitan sucrose fatty acid esters, polyoxyethylene alkyl and alkyl allyl ethers, polyoxyethylene lanolin alcohol, glycerine and polyoxyethylene glycerine fatty acid esters, polyoxyethylene propylene glycol and sorbitol fatty acid esters, polyoxyethylene lanolin, castor oil or hardened castor oil derivatives, polyoxyethylene fatty acid amides, polyoxyethylene alkyl amines, alkylpyrrolidone, glucamides, alkylpolyglucosides, and mono- and dialkanol amides.

Typical fatty acid glycerine and polyglycerine esters, as well as typical sorbitan sucrose fatty acid esters, fatty acid amides, and polyethylene oxide/polypropylene oxide

block copolymers are disclosed by U.S. Patent No. 5,510,042, Hartman et al, incorporated herein by reference.

The castor oil derivatives are typically ethoxylated castor oil. It is noted that other ethoxylated natural fats, oils or waxes are also suitable.

5 Polyoxyethylene fatty acid amides are made by ethoxylation of fatty acid amides with one or two moles of ethylene oxide or by condensing mono-or diethanol amines with fatty acid.

Polyoxyethylene alkyl amines include those of formula:  $\text{RNH}-(\text{CH}_2\text{CH}_2\text{O})_n\text{-H}$ , wherein R is  $\text{C}_6$  to  $\text{C}_{22}$  alkyl and n is from 1 to about 100.

10 Monoalkanol amides include those of formula:  $\text{RCONHR}^1\text{OH}$ , wherein R is  $\text{C}_6$ - $\text{C}_{22}$  alkyl and  $\text{R}^1$  is  $\text{C}_1$  to  $\text{C}_6$  alkylene. Dialkanol amides are typically mixtures of:

diethanolamide:  $\text{RCON}(\text{CH}_2\text{CH}_2\text{OH})_2$ ;

amide ester:  $\text{RCON}(\text{CH}_2\text{CH}_2\text{OH})\text{-CH}_2\text{CH}_2\text{OOCR}$ ;

amine ester:  $\text{RCOOCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{OH}$ ; and

15 amine soap:  $\text{RCOOH}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$ ,

wherein R in the above formulas is an alkyl of from 6 to 22 carbon atoms.

Examples of preferred but not limiting surfactants for detergent bar products are the following.

#### Straight-Chain Primary Alcohol Alkoxylates

20 The deca-, undeca-, dodeca-, tetradeca-, and pentadeca-ethoxylates of n-hexadecanol, and n-hexadecanol, and n-octadecanol having an HLB within the range recited herein are useful nonionics in the context of this invention. Exemplary ethoxylated primary alcohols useful herein as the conventional nonionic surfactants of the compositions are n- $\text{C}_{18}\text{EO}(10)$ ; n- $\text{C}_{14}\text{EO}(13)$ ; and n- $\text{C}_{10}\text{EO}(11)$ . The ethoxylates of  
25 mixed natural or synthetic alcohols in the "tallow" chain length range are also useful herein. Specific examples of such materials include tallow-alcohol-EO(11), tallow-alcohol-EO(18), and tallow-alcohol-EO(25).

#### Straight-Chain Secondary Alcohol Alkoxylates

30 The deca-, undeca-, dodeca-, tetradeca-, pentadeca-, octadeca-, and nonadeca-ethoxylates of 3-hexadecanol, 2-octadecanol, 4-eicosanol, and 5-eicosanol having an HLB within the range recited herein are useful conventional nonionics in the context of this invention. Exemplary ethoxylated secondary alcohols useful herein are 2- $\text{C}_{16}\text{EO}(11)$ ; 2- $\text{C}_{20}\text{EO}(11)$ ; and 2- $\text{C}_{16}\text{EO}(14)$ .

#### Alkyl Phenol Alkoxylates

35 As in the case of the alcohol alkoxylates, the hexa- through octadeca-ethoxylates of alkylated phenols, particularly monohydric alkylphenols, having an HLB within the

range recited herein are useful as conventional nonionic surfactants in the instant compositions. The hexa- through octadeca-ethoxylates of p-tridecylphenol, m-pentadecylphenol, and the like, are useful herein. Exemplary ethoxylated alkylphenols useful in the mixtures herein are: p-tridecylphenol EO(11) and p-pentadecylphenol EO(18). Especially preferred is Nonyl Nonoxynol-49 known as Igepal® DM-880 from Rhone-Poulenc Inc.

As used herein and as generally recognized in the art, a phenylene group in the nonionic formula is the equivalent of an alkylene group containing from 2 to 4 carbon atoms. For present purposes, nonionics containing a phenylene group are considered to contain an equivalent number of carbon atoms calculated as the sum of the carbon atoms in the alkyl group plus about 3.3 carbon atoms for each phenylene group.

#### Olefinic Alkoxylates

The alkenyl alcohols, both primary and secondary, and alkenyl phenols corresponding to those disclosed immediately hereinabove can be ethoxylated to an HLB within the range recited herein and used as the conventional nonionic surfactants of the instant compositions.

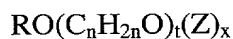
#### Branched Chain Alkoxylates

Branched chain primary and secondary alcohols which are available can be ethoxylated and employed as conventional nonionic surfactants in compositions herein.

The above ethoxylated nonionic surfactants are useful in the present compositions alone or in combination, and the term "nonionic surfactant" encompasses mixed nonionic surface active agents.

#### Alkylpolysaccharides

Still further suitable nonionic surfactants of this invention include alkylpolysaccharides, preferably alkylpolyglycosides of the formula:



wherein

Z is derived from glucose;

R is a hydrophobic group selected from the group consisting of a C<sub>10</sub>-C<sub>18</sub>, preferably a C<sub>12</sub>-C<sub>14</sub>, alkyl group, alkyl phenyl group, hydroxyalkyl group, hydroxyalkylphenyl group, and mixtures thereof;

n is 2 or 3; preferably 2;

t is from 0 to 10; preferably 0; and

x is from 1.5 to 8; preferably 1.5 to 4; more preferably from 1.6 to 2.7.

These surfactants are disclosed in U.S. Patent Nos. 4,565,647, Llenado, issued January 21, 1986; 4,536,318, Cook et al., issued August 20, 1985; 4,536,317, Llenado et



al., issued August 20, 1985; 4,599,188 Llenado, issued July 8, 1986; and 4,536,319, Payne, issued August 20, 1985; all of which are incorporated herein by reference.

The compositions of the present invention can also comprise mixtures of the above nonionic surfactants.

5       A thorough discussion of nonionic surfactants for detergent bar and liquid products is presented by U.S. Patent Nos. 5,510,042, Hartman et al., and 4,483,779, Llenado, et al., incorporated herein by reference.

B.     Anionic Surfactants

10       Anionic surfactants include any of the known hydrophobes attached to a carboxylate, sulfonate, sulfate or phosphate polar, solubilizing group including salts. Salts may be the sodium, potassium, ammonium and amine salts of such surfactants. Useful anionic surfactants can be organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 8 to about 22 carbon atoms and  
15       a sulfonic acid or sulfuric acid ester group, or mixtures thereof. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic deterative surfactants which can be used in the present invention are the alkyl sulfates, especially those obtained by sulfating the higher alcohols (C<sub>8</sub>-C<sub>18</sub> carbon atoms) produced from the glycerides of tallow or coconut oil; and alkyl benzene sulfonates.

20       Other useful anionic surfactants herein include the esters of alpha-sulfonated fatty acids preferably containing from about 6 to 20 carbon atoms in the ester group; 2-acyloxyalkane-1-sulfonic acids preferably containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; alkyl ether sulfates preferably containing from about 10 to 20 carbon atoms in the alkyl group  
25       and from about 1 to 30 moles of ethylene oxide; olefin sulfonates preferably containing from about 12 to 24 carbon atoms; and beta-alkyloxy alkane sulfonates preferably containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

30       Anionic surfactants based on the higher fatty acids, i.e., "soaps" are useful anionic surfactants herein. Higher fatty acids containing from about 8 to about 24 carbon atoms and preferably from about 10 to about 20 carbon atoms and the coconut and tallow soaps can also be used herein as corrosion inhibitors.

35       Preferred water-soluble anionic organic surfactants herein include linear alkyl benzene sulfonates containing from about 10 to about 18 carbon atoms in the alkyl group; branched alkyl benzene sulfonates containing from about 10 to about 18 carbon atoms in the alkyl group; the tallow range alkyl sulfates; the coconut range alkyl glyceryl

sulfonates; alkyl ether (ethoxylated) sulfates wherein the alkyl moiety contains from about 12 to 18 carbon atoms and wherein the average degree of ethoxylation varies between 1 and 12, especially 3 to 9; the sulfated condensation products of tallow alcohol with from about 3 to 12, especially 6 to 9, moles of ethylene oxide; and olefin sulfonates containing from about 14 to 16 carbon atoms.

Specific preferred anionics for use herein include: the linear C<sub>10</sub>-C<sub>14</sub> alkyl benzene sulfonates (LAS); the branched C<sub>10</sub>-C<sub>14</sub> alkyl benzene sulfonates (ABS); the tallow alkyl sulfates, the coconut alkyl glyceryl ether sulfonates; the sulfated condensation products of mixed C<sub>10</sub>-C<sub>18</sub> tallow alcohols with from about 1 to about 14 moles of ethylene oxide; and the mixtures of higher fatty acids containing from 10 to 18 carbon atoms.

It is to be recognized that any of the foregoing anionic surfactants can be used separately herein or as mixtures. Moreover, commercial grades of the surfactants can contain non-interfering components which are processing by-products. For example, commercial alkaryl sulfonates, preferably C<sub>10</sub>-C<sub>14</sub>, can comprise alkyl benzene sulfonates, alkyl toluene sulfonates, alkyl naphthalene sulfonates and alkyl poly-benzenoid sulfonates. Such materials and mixtures thereof are fully contemplated for use herein.

Other examples of the anionic surfactants used herein include fatty acid soaps, ether carboxylic acids and salts thereof, alkane sulfonate salts, *α*-olefin sulfonate salts, sulfonate salts of higher fatty acid esters, higher alcohol sulfate ester or ether ester salts, alkyl, preferably higher alcohol phosphate ester and ether ester salts, and condensates of higher fatty acids and amino acids.

Fatty acid soaps include those having the formula: R-C(O)OM, wherein R is C<sub>6</sub> to C<sub>22</sub> alkyl and M is preferably sodium.

Salts of ether carboxylic acids and salts thereof include those having the formula: R-(OR<sup>1</sup>)<sub>n</sub>-OCH<sub>2</sub>C(O)OM, wherein R is C<sub>6</sub> to C<sub>22</sub> alkyl, R<sup>1</sup> is C<sub>2</sub> to C<sub>10</sub>, preferably C<sub>2</sub> alkyl, and M is preferably sodium.

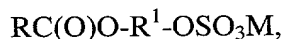
Alkane sulfonate salts and *α*-olefin sulfonate salts have the formula: R-SO<sub>3</sub>M, wherein R is C<sub>6</sub> to C<sub>22</sub> alkyl or *α*-olefin, respectively, and M is preferably sodium.

Sulfonate salts of higher fatty acid esters include those having the formula:



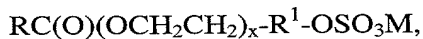
wherein R is C<sub>12</sub> to C<sub>22</sub> alkyl, R<sup>1</sup> is C<sub>1</sub> to C<sub>18</sub> alkyl and M is preferably sodium.

Higher alcohol sulfate ester salts include those having the formula:



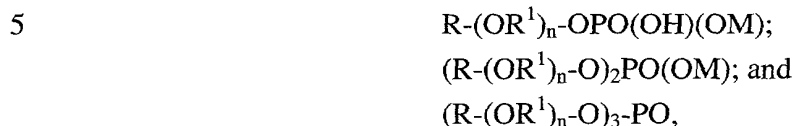
wherein R is C<sub>12</sub>-C<sub>22</sub> alkyl, R<sup>1</sup> is C<sub>1</sub>-C<sub>18</sub> hydroxyalkyl, M is preferably sodium.

Higher alcohol sulfate ether ester salts include those having the formula:



wherein R is C<sub>12</sub>-C<sub>22</sub> alkyl, R<sup>1</sup> is C<sub>1</sub>-C<sub>18</sub> hydroxyalkyl, M is preferably sodium and x is an integer from 5 to 25.

Higher alcohol phosphate ester and ether ester salts include compounds of the formulas:



wherein R is alkyl or hydroxyalkyl of 12 to 22 carbon atoms, R<sup>1</sup> is C<sub>2</sub>H<sub>4</sub>, n is an integer from 5 to 25, and M is preferably sodium.

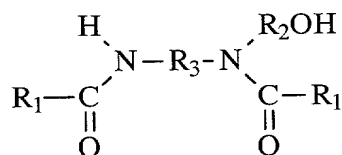
10            Other anionic surfactants herein are sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates containing from about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl groups contain from about 8 to about 12 carbon atoms; and sodium or potassium salts of alkyl ethylene oxide ether sulfates containing about 1 to about 10 units  
15 of ethylene oxide per molecule and wherein the alkyl group contains from about 10 to about 20 carbon atoms.

C.      Cationic Surfactants

Preferred cationic surfactants of the present invention are the reaction products of higher fatty acids with a polyamine selected from the group consisting of  
20 hydroxyalkylalkylenediamines and dialkylenetriamines and mixtures thereof.

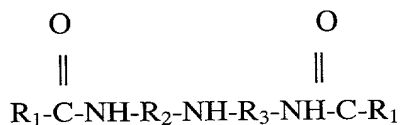
A preferred component is a nitrogenous compound selected from the group consisting of:

- (i) the reaction product mixtures of higher fatty acids with hydroxyalkylalkylenediamines in a molecular ratio of about 2:1, said reaction product containing a composition having a compound of the formula:



wherein R<sub>1</sub> is an acyclic aliphatic C<sub>15</sub>-C<sub>21</sub> hydrocarbon group and R<sub>2</sub> and R<sub>3</sub> are divalent C<sub>1</sub>-C<sub>3</sub> alkylene groups; commercially available as Mazamide 6 from PPG;

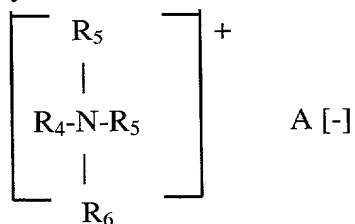
- (ii) the reaction product of higher fatty acids with dialkylenetriamines in a molecular ratio of about 2:1; said reaction product containing a composition having a compound of the formula:



wherein R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are as defined above; and mixtures thereof.

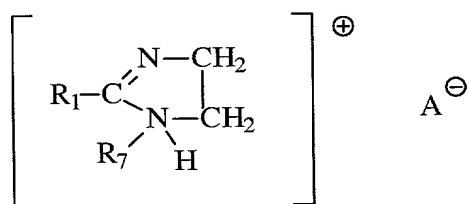
Another preferred component is a cationic nitrogenous salt containing one long chain acyclic aliphatic C<sub>15</sub>-C<sub>22</sub> hydrocarbon group selected from the group consisting of:

- (i) acyclic quaternary ammonium salts having the formula:



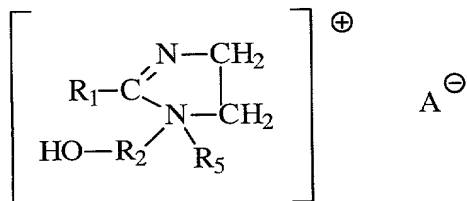
wherein  $R_4$  is an acyclic aliphatic  $C_{15}$ - $C_{22}$  hydrocarbon group,  $R_5$  and  $R_6$  are  $C_1$ - $C_4$  saturated alkyl or hydroxyalkyl groups, and  $A^-$  is an anion, especially as described in more detail hereinafter, examples of these surfactants are sold by Sherex Chemical Company under the Adgen trademarks;

- (ii) substituted imidazolinium salts having the formula:



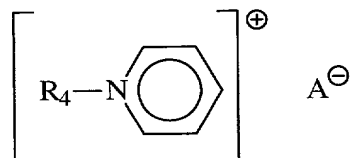
wherein  $R_1$  is an acyclic aliphatic  $C_{15}$ - $C_{21}$  hydrocarbon group,  $R_7$  is a hydrogen or a  $C_1$ - $C_4$  saturated alkyl or hydroxyalkyl group, and  $A^-$  is an anion;

- (iii) substituted imidazolinium salts having the formula:



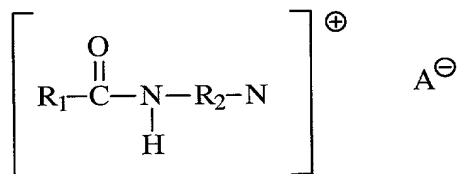
wherein  $R_2$  is a divalent  $C_1$ - $C_3$  alkylene group and  $R_1$ ,  $R_5$  and  $A^-$  are as defined above; an example of which is commercially available under the Monaquat ISIES trademark from Mona Industries, Inc.;

- (iv) alkyipyridinium salts having the formula:



wherein R<sub>4</sub> is an acyclic aliphatic C<sub>16</sub>-C<sub>22</sub> hydrocarbon group and A [-] is an anion; and

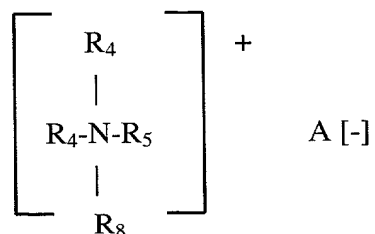
- (v) alkanamide alkylene pyridinium salts having the formula:



wherein R<sub>1</sub> is an acyclic aliphatic C<sub>15</sub>-C<sub>21</sub> hydrocarbon group, R<sub>2</sub> is a divalent C<sub>1</sub>-C<sub>3</sub> alkylene group, and A [-] is an anion group; and mixtures thereof.

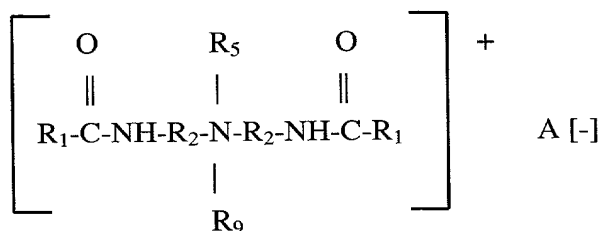
Another class of preferred cationic nitrogenous salts having two or more long chain acyclic aliphatic C<sub>15</sub>-C<sub>22</sub> hydrocarbon groups or one said group and an arylalkyl group are selected from the group consisting of:

- (i) acyclic quaternary ammonium salts having the formula:



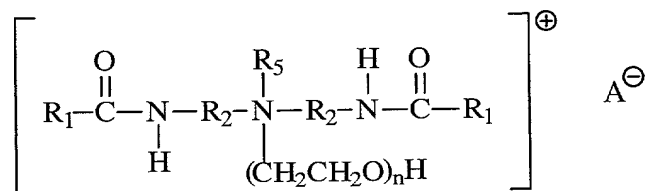
wherein each  $R_4$  is an acyclic aliphatic  $C_{15}$ - $C_{22}$  hydrocarbon group,  $R_5$  is a  $C_1$ - $C_4$  saturated alkyl or hydroxyalkyl group,  $R_8$  is selected from the group consisting of  $R_4$  and  $R_5$  groups, and  $A^-$  is an anion defined as above; examples of which are commercially available from Sherex Company under the Adgen trademarks;

- (ii) diamido quaternary ammonium salts having the formula:



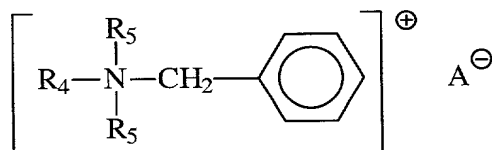
wherein each  $R_1$  is an acyclic aliphatic  $C_{15}$ - $C_{21}$  hydrocarbon group,  $R_2$  is a divalent alkylene group having 1 to 3 carbon atoms,  $R_5$  and  $R_9$  are  $C_1$ - $C_4$  saturated alkyl or hydroxyalkyl groups, and  $A^-$  is an anion; examples of which are sold by Sherex Chemical Company under the Varisoft trademark;

- (iii) diamino alkoxyated quaternary ammonium salts having the formula:



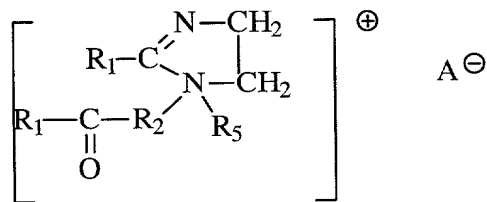
wherein n is equal to 1 to about 5, and R<sub>1</sub>, R<sub>2</sub>, R<sub>5</sub> and A [-] are as defined above;

- iv) quaternary ammonium compounds having the formula:



wherein each R<sub>4</sub> is an acyclic aliphatic C<sub>15</sub>-C<sub>22</sub> hydrocarbon group, each R<sub>5</sub> is a C<sub>1</sub>-C<sub>4</sub> saturated alkyl or hydroxyalkyl group, and A [-] is an anion; examples of such surfactants are available from Onyx Chemical Company under the Ammonyx<sup>®</sup> 490 trademark;

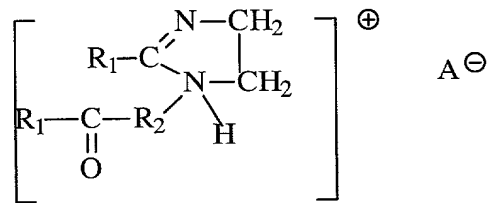
- (v) substituted imidazolinium salts having the formula:



wherein each R<sub>1</sub> is an acyclic aliphatic C<sub>15</sub>-C<sub>21</sub> hydrocarbon group, R<sub>2</sub> is a divalent alkylene group having 1 to 3 carbon atoms, and R<sub>5</sub> and A [-] are as defined above; examples are commercially available from Sherex Chemical Company under the Varisoft 475 and Varisoft 445 trademarks; and



(vi) substituted imidazolinium salts having the formula:



wherein R<sub>1</sub>, R<sub>2</sub> and A - are as defined above; and mixtures thereof.

The more preferred cationic conventional surfactant is selected from the group consisting of an alkyltrimethylammonium salt, a dialkyldimethylammonium salt, an alkyldimethylbenzylammonium salt, an alkyipyridinium salt, an alkylisoquinolinium salt, benzethonium chloride, and an acylamino acid cationic surfactant.

#### Anion A

In the cationic nitrogenous salts herein, the anion A [-] provides electrical neutrality. Most often, the anion used to provide electrical neutrality in these salts is a halide, such as chloride, bromide, or iodide. However, other anions can be used, such as methylsulfate, ethylsulfate, acetate, formate, sulfate, carbonate, and the like. Chloride and methylsulfate are preferred herein as anion A.

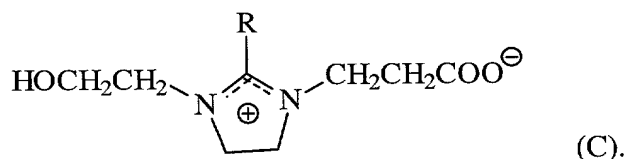
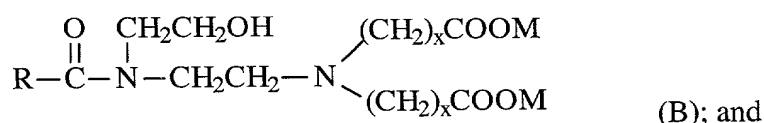
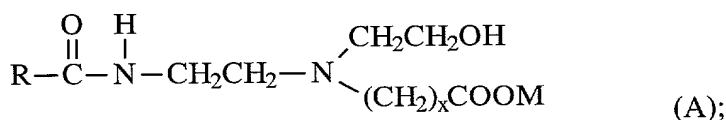
Cationic surfactants are commonly employed as fabric softeners in compositions added during the rinse cycle of clothes washing. Many different types of fabric conditioning agents have been used in rinse cycle added fabric conditioning compositions as disclosed by U.S. Patent No. 5,236,615, Trinh et al. and U.S. Patent No. 5,405,542, Trinh et al., both patents herein incorporated by reference in their entirety. The most favored type of agent has been the quaternary ammonium compounds. Many such quaternary ammonium compounds are disclosed for example, by U.S. Patent No. 5,510,042, Hartman et al. incorporated herein by reference in its entirety. These compounds may take the form of noncyclic quaternary ammonium salts having preferably two long chain alkyl groups attached to the nitrogen atoms. Additionally, imidazolinium salts have been used by themselves or in combination with other agents in the treatment of fabrics as disclosed by U.S. Patent No. 4,127,489, Pracht, et al., incorporated herein by reference in its entirety. U.S. Patent No. 2,874,074, Johnson discloses using imidazolinium salts to condition fabrics; and U.S. Patent No. 3,681,241, Rudy, and U.S. Patent No. 3,033,704, Sherrill et al. disclose fabric conditioning compositions containing mixtures of imidazolinium salts and other fabric conditioning agents. These patents are incorporated herein by reference in their entirety.

D. Amphoteric Surfactants

Amphoteric surfactants have a positive or negative charge or both on the hydrophilic part of the molecule in acidic or alkaline media.

Examples of the amphoteric surfactants which can be used herein include amino acid, betaine, sultaine, phosphobetaines, imidazolinium derivatives, soybean phospholipids, and yolk lecithin. Examples of suitable amphoteric surfactants include the alkali metal, alkaline earth metal, ammonium or substituted ammonium salts of alkyl amphocarboxy glycines and alkyl amphocarboxypropionates, alkyl amphodipropionates, alkyl amphodiacetates, alkyl amphoglycines and alkyl amphopropionates wherein alkyl represents an alkyl group having 6 to 20 carbon atoms. Other suitable amphoteric surfactants include alkyliminopropionates, alkyl iminodipropionates and alkyl amphopropylsulfonates having between 12 and 18 carbon atoms, alkylbetaines and amidopropylbetaines and alkylsultaines and alkylamidopropylhydroxy sultaines wherein alkyl represents an alkyl group having 6 to 20 carbon atoms are especially preferred.

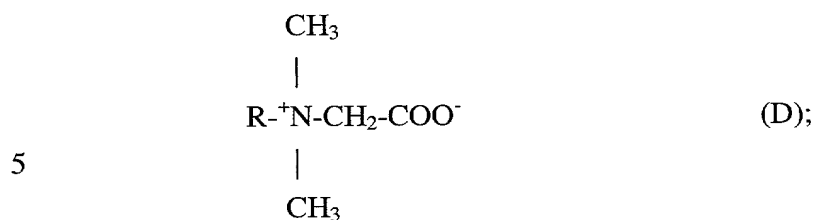
Particularly useful amphoteric surfactants include both mono and dicarboxylates such as those of the formulae:



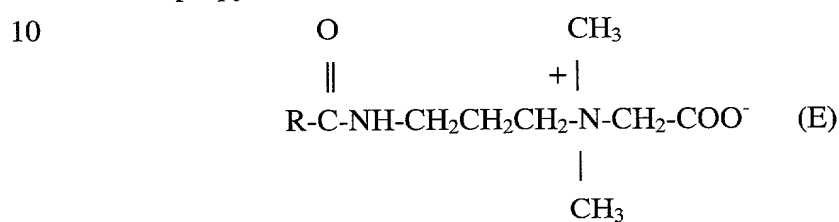
wherein R is an alkyl group of 6-20 carbon atoms, x is 1 or 2 and M is hydrogen or sodium. Mixtures of the above structures are particularly preferred.

Other formulae for the above amphoteric surfactants include the following:

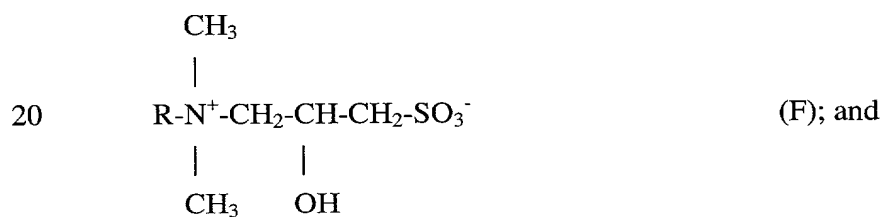
Alkyl betaines



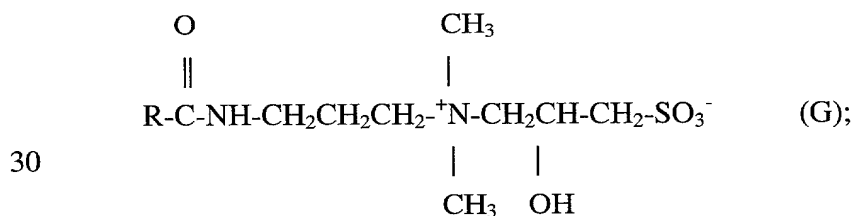
Amidopropyl betaines



Alkyl sultaines



Alkyl amidopropylhydroxy sultaines



where R is an alkyl group of 6-20 carbon atoms and M is hydrogen or sodium.

Of the above amphoteric surfactants, particularly preferred are the alkali salts of alkyl amphocarboxyglycinates and alkyl amphocarboxypropionates, alkyl amphodipropionates, alkyl amphodiacetates, alkyl amphoglycinates, alkyl amphopropyl

- sulfonates and alkyl amphopropionates wherein alkyl represents an alkyl group having 6 to 20 carbon atoms. Even more preferred are compounds wherein the alkyl group is derived from coconut oil or is a lauryl group, for example, cocoamphodipropionate. Such cocoamphodipropionate surfactants are commercially sold under the trademarks Miranol C2M-SF CONC. and Miranol FBS by Rhone-Poulenc Inc.

Other commercially useful amphoteric surfactants are available from Rhone-Poulenc Inc. and include:

cocoamphoacetate (sold under the trademarks MIRANOL CM CONC. and MIRAPON FA),
cocoamphopropionate (sold under the trademarks MIRANOL CM-SF CONC. and MIRAPON FAS),
cocoamphodiacetate (sold under the trademarks MIRANOL C2M CONC. and MIRAPON FB),
lauroamphoacetate (sold under the trademarks MIRANOL HM CONC. and MIRAPON LA),
lauroamphodiacetate (sold under the trademarks MIRANOL H2M CONC. and MIRAPON LB),
lauroamphodipropionate (sold under the trademarks MIRANOL H2M SF CONC. AND MIRAPON LBS),
lauroamphodiacetate obtained from a mixture of lauric and myristic acids (sold under the trademark MIRANOL BM CONC.), and
cocoamphopropyl sulfonate (sold under the trademark MIRANOL CS CONC.)

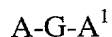
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Somewhat less preferred are:

caproamphodiacetate (sold under the trademark MIRANOL S2M CONC.),
caproamphoacetate (sold under the trademark MIRANOL SM CONC.),
caproamphodipropionate (sold under the trademark MIRANOL S2M-SF CONC.), and
stearoamphoacetate (sold under the trademark MIRANOL DM).

E. Gemini Surfactants

Gemini surfactants form a special class of surfactant. These surfactants have the general formula:



and get their name because they comprise two surfactant moieties ( $A, A^1$ ) joined by a spacer (G), wherein each surfactant moiety ( $A, A^1$ ) has a hydrophilic group and a hydrophobic group. Generally, the two surfactant moieties ( $A, A^1$ ) are twins, but they can be different.

The gemini surfactants are advantageous because they have low critical micelle concentrations (cmc) and, thus, lower the cmc of solutions containing both a gemini surfactant and a conventional surfactant. Lower cmc causes better solubilization and increased detergency at lower surfactant use levels and unexpectedly enhances the deposition of the soil release polymers as claimed by this invention with demonstrated results to follow herein. Soil removal agents adhere to the fabric being laundered, much better than when mixed with only non-gemini, conventional surfactants.

Also, the gemini surfactants result in a low  $pC_{20}$  value and low Krafft points. The  $pC_{20}$  value is a measure of the surfactant concentration in the solution phase that will reduce the surface tension of the solvent by 20 dynes/cm. It is a measure of the tendency of the surfactant to adsorb at the surface of the solution. The Krafft point is the temperature at which the surfactant's solubility equals the cmc. Low Krafft points imply better solubility in water, and lead to greater latitude in making formulations.

A number of the gemini surfactants are reported in the literature, see for example, Okahara et al., J. Japan Oil Chem. Soc. 746 (Yukagaku) (1989); Zhu et al., 67 JAOCS 7,459 (July 1990); Zhu et al., 68 JAOCS 7,539 (1991); Menger et al., J. Am. Chemical Soc. 113, 1451 (1991); Masuyama et al., 41 J. Japan Chem. Soc. 4,301 (1992); Zhu et al., 69 JAOCS 1,30 (Jan. 1992); Zhu et al., 69 JAOCS 7,626 July 1992); Menger et al., 115 J. Am. Chem. Soc. 2, 10083 (1993); Rosen, Chemtech 30 (March 1993); and Gao et al., 71 JAOCS 7,771 (July 1994), all of this literature incorporated herein by reference.

Also, gemini surfactants are disclosed by U.S. Patent Nos. 2,374,354, Kaplan; 2,524,218, Bersworth; 2,530,147 Bersworth (two hydrophobic tails and three hydrophilic heads); 3,244,724, Guttman; 5,160,450, Okahara, et al., all of which are incorporated herein by reference.

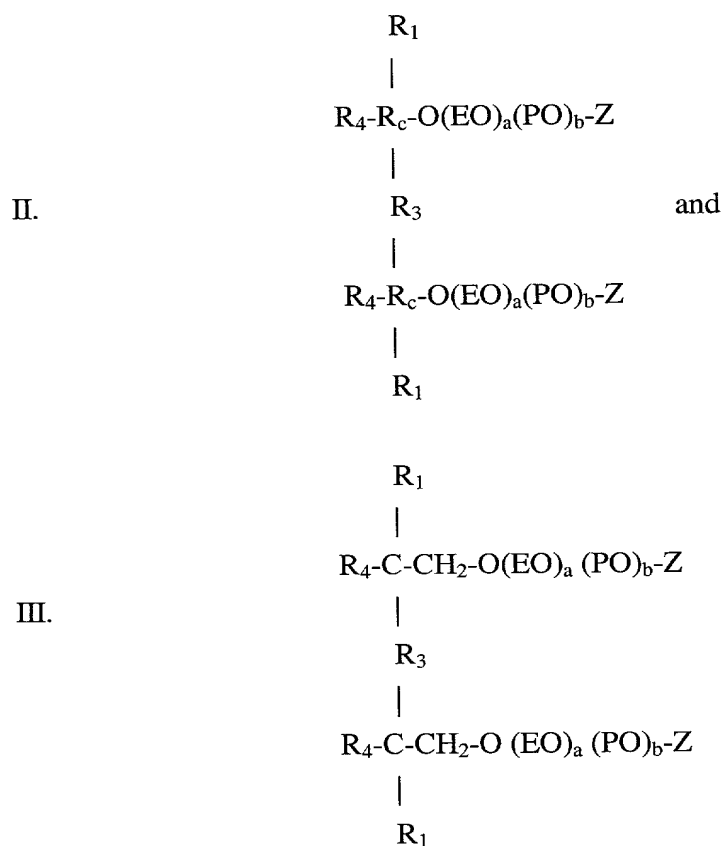
The gemini surfactants may be anionic, nonionic, cationic or amphoteric. The hydrophilic and hydrophobic groups of each surfactant moiety ( $A, A^1$ ) may be any of those

known to be used in conventional surfactants having one hydrophilic group and one hydrophobic group.

For example, a typical nonionic gemini surfactant, e.g., a bis-polyoxyethylene alkyl ether, would contain two polyoxyethylene alkyl ether moieties.

5 Each moiety would contain a hydrophilic group, e.g., polyethylene oxide, and a hydrophobic group, e.g., an alkyl chain.

Gemini surfactants specifically useful in the present invention include gemini anionic or nonionic surfactants of the formulae:



wherein  $\text{R}_c$  represents aryl, preferably phenyl.